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The effects of various chemical treatments on the surface area of coals

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Surface areas of most American coals are small when measured by N_2 adsorption at 77 K and large when measured by CO_2 adsorption at 298 K, implying that the majority of the pores are less then 5 Å in diameter. This small pore size would restrict many gaseous and liquid reactants from entering the internal pore system of the coal, and hence, reduces the efficiency of coal conversion. Therefore, if

the surface area, as measured by N_2 (77 K), could be increased, that is, to increase the pore size, the conversion of coal into useful products should be accomplished more efficiently.

Determining the surface properties of coal during treatment is important if one wishes to maximize any future process. Therefore, this research project is undertaken to gain knowledge of the surface properties (in particular the surface area) of coals undergoing treatment with various gaseous and liquid reactants. In particaular, the effects of heat treatment in a stream of N_2 up to 600°C and of oxidation in a stream of O_2:N_2 (5%:95%) at various temperatures between 350° and 450°C are studied with three coals of various ranks. The effect of pyridine extraction, at room temperature, before heat and oxidation treatments are examined for two of the coals, in addition to treatment with chromyl chloride at 100°C. Finally, the effects of hydrogen and oxygen atoms on the surface area of the coals are also investigated.

During the course of theis work, it was noticed that time, at ambient conditions, played a role on the newly created surface area following the oxygen-nitrogen treatment. The decrease in the surface area, as time increases at ambient conditions was investigated for all three coals.

The adsorption of N_2 at 77 K and of CO_2 at 196 and 298 K were measured on either a volumetric or a thermal

apparatus, and the BET or the Dubinin-Polanyi equations were used to calculate the surface area. The three coals used in this study were: PSOC 379, a semi-anthracite; PSOC 190, a bituminous HVC; and PSOC 371, a bituminous HVA.

The heat treatments in N_2 were done at 350°, 375°, 400°, 500° and 600°C for PSOC 371 and at the latter four temperatures for PSOC 379 and PSOC 190. The surface area, as measured by CO_2 (298 K), for these chars increased up to 600°C and the surface area, as measured by N_2 (77 K), had changed little.

The oxygen-nitrogen treatments were done at 350°, 375°, and 400°C for PSOC 371; at 375°, 400°, 425° and 450°C for PSOC 379 and at 350°, 375°, 400° and 425°C for PSOC 190. The surface area, as measured by N_2 (77 K), after these treatments had significantly increased over the heat treated samples at temperatures of 400°C for PSOC 371 and PSOC 190 and at 450°C for PSOC 379.

When PSOC 371 and PSOC 190 were first treated with pyridine and then with heat and oxygen-nitrogen at 400°C, it was found that the surface area, as measured by N_2 (77 K), was less than the oxidative treatment of the raw coal. It is possible that the use of other solvents and/or the extraction at higher temperatures with pyridine might prove fruitful.

Chromyl chloride treatment followed by heating to 450°C and treatment, up to 4 hours, with hydrogen and oxygen

atoms had failed to increase the surface area, as measured by N_2 (77 K).

THE EFFECTS OF VARIOUS CHEMICAL TREATMENTS ON THE SURFACE AREA OF COALS

by

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INTRODUCTION

Background

Coal is formed from plant debris which has been modified by both chemical and physical means. Many factors affect the composition of coals and a few are: the mode of accumulation and burial of deposits, the age and geographical distribution of the deposits, the structure of the plants that form the deposits, the type and amount of the plant decaying agents and the subsequent geological history of the residual decay products (1). This gives coal a complex heterogeneous composition of organic and inorganic substances with varying physical properties.

Coals have aromatic and hydroaromatic building blocks with a varying amount of cross-linkages. From extensive x-ray studies, Hirsch (2) has described three types of structures for a wide range of coals. These structures are: (i) open structure, (ii) liquid structure and (iii) anthracite structures. The first of these structures is characteristic of lower ranked coals; having a carbon content up to 85%, are highly porous with cross-links between lamellae which are randomly oriented. The liquid structure is descriptive of bituminous coals; carbon content between 85 and 91%, with a reduced number of cross-links and formation

of groups of lamellae layers parallel to each other. The number of macropores present here are few. The anthracite structure is typical of higher ranked coals; carbon content greater then 91%, the lamellae here are not cross-linked but highly oriented toward each other. This higher orientation results in an increase in porosity over the liquid structure.

The pores in coals can be of varying size and the distribution of pore sizes affects the pore surface area. Dubinin (3) has suggested a classification for pore sizes, in porous adsorbents, as: (i) micropores, diameters less then 20 $\mathring{A}$; (ii) transitional pores, diameters between 20 and 200 $\mathring{A}$; and (iii) macropores, diameters larger then 200 $\mathring{A}$. However, Gan, Nandi and Walker (4) use 12 and 300 $\mathring{A}$ for the dividing lines between the three sizes.

The porosity in coals affects the mining, preparation and utilization of coals and has its greatest effect on the utilization processes. In the gasification or liquefaction of coals, chemical reactions must occur with the surface of the coal, where most of the surface is in the pore structure. The products, formed from the chemical reactions, must be able to leave the pores efficiently in order for fresh reactant molecules to enter. Since most of these processes occur with thermal heating, chars are intermediate products with important characteristics.

Gan, Nandi and Walker (4) studied several American coals and their pore structure using the following techniques: gas adsorption, helium and mercury displacement and

mercury porosimetry. They found that the surface areas, from carbon dioxide adsorption at 298 K, were between 100 and 426 m^2g^{-1} and the surface areas, from nitrogen adsorption at 77 K, were mostly less then 1 m^2g^{-1}, showing the molecular sieve property of coals.

The surface area of coal changes when it is treated with heat or chemicals and this change is of importance in the processing of coal. When coal is heated, volatile matter is released from the framework and additional porosity and surface area are formed. However, after a certain temperature the cross-links are broken and the result is a collapse of the structural framework leading to a loss of porosity and surface area. Therefore, there will be a temperature where the surface area will reach a maximum during the heating process.

Toda (5) studied the changes in the density, that is the change in the pore structure, of 12 coals upon heat treatment to a temperature of 1200°C. Since there was only slight changes in the densities up to 350°C, Toda concluded that there was only dehydration and no significant structural changes, but above 350°C the specific volume decreased indicating changes in the micropore structure of the coals studied. The temperature of maximum density depended on the rank of the coal. Changes of the surface area of coals during heat treatment have been examined by several workers (6, 7, 8). Their work showed that the temperature for

maximum surface area was affected by the nature of the coal.

Since many of the lower ranked coals are caking upon heat treatment, which is an undesirable property, the benefits of preoxidation of the coals have been examined by many workers. Mahajan and co-workers (9) showed that the preoxidation of two caking coals between 180° and 250°C and its subsequent heat treatment in nitrogen up to 1000°C, increased the surface area, as measured by CO_2 adsorption at 298 K. Oda and fellow workers (10) looked at the changes in the pore structure of air-oxidized coals and cokes or chars. They found that the pore-volume increases at 400°C; reaches a maximum at 700°C, for low ranked coals, after which it sharply decreases. The pore-volume change upon heat treatment depends on the coal rank and the degree of preoxidation. In all but one case, the air-oxidized samples had a larger pore-volume then the parent coal.

Solvent extraction of coal can also markedly affect the surface areas of coals. Medeiros and Petersen (11) examined the effects of progressive extraction on a subbituminous coal and found that the surface areas, as measured by CO_2 adsorption at 196 K, varied with extraction time, temperature, yield and the nature of the solvent. The maximum surface area obtained by these authors was 265 m^2g^{-1} from a four hour treatment using tetralin at 350°C (the raw coal has a surface area of 99 m^2g^{-1} as measured by CO_2 at 196 K). Booras and Petersen (12) examined the effects of pyridine extraction on a subbituminous coal from 100°C to

300°C in a pressurized refluxed extraction apparatus. They found that with a four hour treatment, the maximum surface area, as measured by CO_2 at 196 K, occurred at 300°C. The surface area was 296 m^2g^{-1}, an increase from the raw coal sample of 84 m^2g^{-1}. The effect of solvent extraction followed by heat treatment has not been investigated.

The reaction of coal and other carbon materials in a microwave discharge of hydrogen, water vapor, argon and carbon dioxide has been investigated by several workers (13, 14, 15, 16). However, only the amount of gasification and the gaseous products were examined and not the resulting chars and accompanying surface areas.

Purpose and Significance

The surface areas, as measured by N_2 at 77 K, of most American coals are small compared to the surface areas, as measured by CO_2 at 196 or 298 K, implying that most pores are smaller than 5 Å in size. It would be profitable to increase the accessibility of reactant gases and liquids, that is, to increase the pore sizes above 5 Å via a pretreatment process. Increasing the pore size should increase the reactivity of the coals and aid in the process of converting coal into useful products.

Providing a means of increasing the pore size of coals would mean a more economical conversion of coal into gaseous or liquid products, and this in turn would minimize our dependence on foreign crude oil as a source of gasoline and

other chemical products. Besides, coal is more evenly distributed over the globe then oil, and this could decrease the strong hold that certain countries have on the world's current major energy and chemical source. The surface properties of the coal during treatment are also important and necessary to maximize the efficiency of the conversion process.

This research project was undertaken to gain more knowledge of the surface area of coals undergoing treatment by gaseous and liquid reactants. In particular, the effects of oxygen-nitrogen at various temperatures on the surface areas of three coals of differing ranks, an extension and review of Salvador Leon Arredondo's work (17), and the heat treatment of the coals in a nitrogen atmosphere up to 600°C were studied. The effect of pyridine extraction before heat treatment and oxidation was investigated for two of the coals in addition to treatment with chromyl chloride at 100°C. Finally, hydrogen and oxygen atom effect on the surface areas were examined.

In the course of this work, it was also noticed that time played a role on the newly created surface areas after the oxygen-nitrogen pretreatment. This effect of surface area decrease, as time increases, was investigated for all three coals and the results are discussed in Chapter 3.

CHAPTER II

EXPERIMENTAL

Surface Area Measurements

A simple method for calculating the surface area of porous material, involving the use of adsorption isotherms, was developed by Brunauer, Emmett and Teller (18, 19, 20), BET. The theory is based on multimolecular adsorption and for a complete derivation see Brunauer, Emmett and Teller (19). The resulting equation is:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\cdot\frac{P}{P_o} \qquad (1)$$

Where:

P = equilibrium pressure

P_o = saturation pressure of the gas at temperature T(K)

V = volume of gas adsorbed at P(STP)

V_m = monolayer volume (STP)

C = a constant related to the heats of liquefaction, E_L, and adsorption, E_1, by the following equation

$C = c \exp[(E_1 - E_L)/RT]$

where c is a constant usually equal to unity. From equation (1), the plot of $P/V(P_o-P)$ against P/P_o results in a straight line in the relative pressure range of 0.05 to 0.30 with the slope equal to $(C-1)/V_mC$ and the intercept equal to $1/V_mC$. Therefore, from the slope and intercept, the values of V_m

and C can be determined.

The number of molecules of adsorbed gas is calculated from the monolayer volume, and multiplication by the cross-sectional area of the adsorbate yields the absolute surface area of the adsorbent. Emmett and Brunauer (18) calculated the area of an adsorbate molecule, assuming a close-packed hexagonal arrangement, from the following equation:

$$\text{Area} = 3.464\ (M/4\sqrt{2}\cdot AD)^{2/3} \qquad (3)$$

Where M is the molecular weight of the adsorbate, A is Avogadro's number and D is the density of the liquefied or solidified adsorbate. Using nitrogen as the adsorbate, at 77 K, the area the molecule occupies is equal to 16.2 Å^2 and for carbon dioxide at 195 and 298 K, the area is equal to 17 and 25.3 Å^2, respectively. These molecular areas are constants and can be converted into another constant, s, using equation (4), so as to make calculations of the surface area easier.

$$s = \frac{A \cdot \text{Area}}{2.24 \times 10^8} \qquad (4)$$

The values of s for nitrogen at 77 K and for carbon dioxide at 195 and 298 K are 4.38, 4.56 and 6.8, respectively. The equation for the surface area, in square meters per gram, is therefore:

$$S = sV_m/m \qquad (5)$$

Where S is the surface area in m^2g^{-1}, s as defined above, V_m is the monolayer volume (STP) and m is the mass, in grams, of the adsorbent.

Since coal is microporous and behaves like a molecular sieve, the adsorption of carbon dioxide at 298 K exceeds the nitrogen adsorption at 77 K. It has been proposed that the diffusion of nitrogen at low temperatures is slow, that is, it is an activated diffusion process and therefore, carbon dioxide adsorption gives a more realistic value of the total surface area (8, 21, 22). However, the saturation vapor pressure of carbon dioxide at 298 K is 63.5 atmospheres and a high pressure apparatus is needed to calculate the surface area from the BET equation. But, Marsh and Siemieniewska (23) calculated the surface area of coals from carbon dioxide adsorption at 0^{o} and $20^{o}C$ using the Dubinin-Polanyi (D-P) equation and a low pressure apparatus. Walker and Patel (24) also compared the surface areas of several coals using a high pressure apparatus and the BET equation, and also using a low pressure apparatus and the D-P equation. The surface area values obtained from both methods were in good agreement. Therefore, they suggested using the D-P equation in a low pressure apparatus for the calculation of the surface area at 298 K using CO_2. The D-P equation is:

$$\log V = \log V_o - \frac{BT^2}{\beta} [\log (P_o/P)]^2 \qquad (6)$$

Where:

V = volume adsorbed at equilibrium pressure P

V_o = micro-pore capacity

P_o = saturation vapor pressure of adsorbate at temperature T

B = a constant

β = affinity coefficient of adsorbate relative to nitrogen

It is seen that from equation (6) a plot of log V against $[\log(P_o/P)]^2$ is linear with the intercept equal to log V_o. If the adsorption of carbon dioxide is restricted to a monolayer, then the intercept, log V_o, is also a measure of the monolayer volume V_m, and then equation (5) can be used to calculate the surface area.

Apparatus and Materials

There are three general systems used for measuring the adsorption of gases: (1) gravimetric, (2) volumetric and (3) thermal conductivity. The latter two methods are used in this work and are presented below.

Volumetric Apparatus. A typical volumetric apparatus is pictured in Figure 1 (17) and consists of:

- a sample adsorption bulb S
- a calibrated gas buret B
- a mercury manometer M
- a Cenco high vacuum mechanical pump
- an oil diffusion pump
- a Televac vacuum gauge

Its use is described by Emmett (20) and others (17, 25, 26) and is easy to operate. Following is a description of the operating procedures.

The first step is to calibrate the free volume, V_o, of

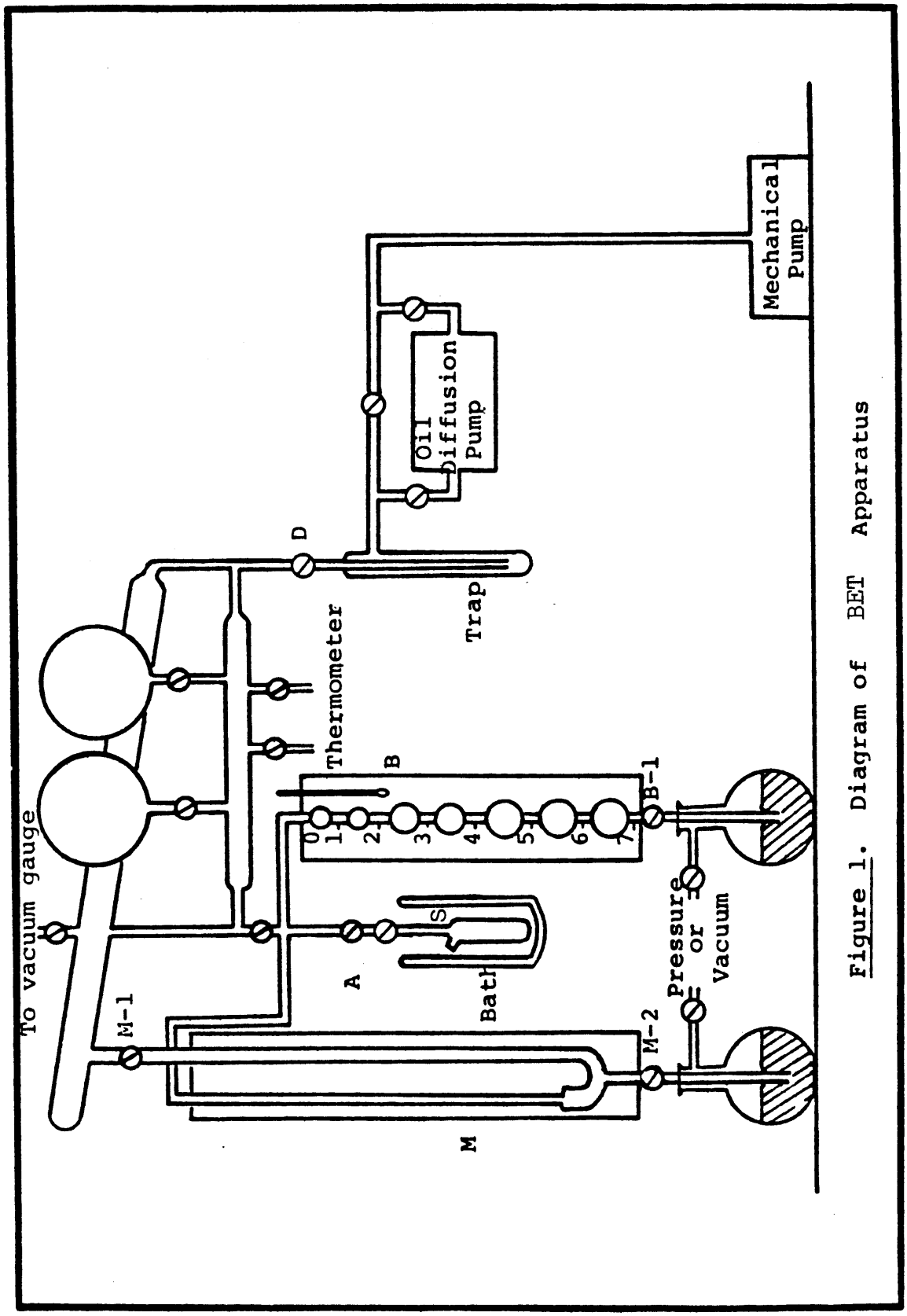

Figure 1. Diagram of BET Apparatus

the system. This consists of the volume between stopcock A, the zero reference of the manometer, to the top of the burette bulbs. The volume of the bulbs are already known from mercury calibration and so with stopcock A closed, one adds enough helium to give a pressure reading of around 760 mm-Hg; an accurate reading of the pressure with the mercury in the manometer at the reference point is recorded and then the mercury is lowered in the burette bulbs to reference line one; the pressure is again recorded. This procedure is repeated until the mercury is lowered to the last reference line. Since the amount of gas is constant, and assuming a constant temperature,

$$PV = \text{constant} = K$$

$$\text{but } V = V_o + V_{empty}$$

$$PV = PV_o + PV_{empty} = K$$

$$\text{or } PV_{empty} = K - PV_o$$

$$\text{therefore } \frac{d(PV_{empty})}{dP} = -V_o$$

The plot of PV_{empty} against P, for each reference line, gives a straight line with slope equal to $-V_o$.

Now, since V_o is known, it is easy to calculate the cumulative volume to each reference line and this is known as the volume factor, V_f. The gas in the system is always corrected to STP and so it saves time to multiply the volume factors by 273.15/760. The volume of any gas, in the system, for which the pressure, P, and the temperature, T, has been determined is:

$V(STP) = V_f(P/T)$

Once the system is calibrated, adsorption measurements can proceed. The sample is placed in the sample bulb and degassed at 130°C for three hours at a pressure less than five microns. It is cooled to room temperature and further degassed, at least 15 hours, at a pressure less than one micron. One should make sure that there are no leaks and that the sample is completely degassed by closing off stopcock D. If the pressure is still below one micron after 15 minutes, then one can proceed with the measurements.

The "dead space" or void space must be calculated first so that one knows the space not taken up by the sample in the sample bulb and helium is used for this purpose. With stopcock A closed, helium is introduced into the system and the pressure is measured at several reference lines. The average of the volumes thus calculated gives V_T, the total volume of gas. Then, stopcock A is opened and helium is admitted into the sample bulb surrounded by a constant temperature bath of 298, 195 or 77 K. A new pressure reading is taken and the volume of helium left in the burette system is calculated and designated as V_R, equal to V_fP/T. The volume that entered the sample bulb is the difference between V_T and V_R, and is designated as V_A, at STP since both V_T and V_R are at STP. The procedure is repeated at several other reference lines. Since V_A varies with pressure, it is easier to assign a bulb factor, f_B, which is equal to

V_A divided by the pressure at each respective reference line. The bulb factor is a constant and multiplication of f_B by the pressure at any time gives the volume of gas, at STP, in the sample bulb.

Now that the volume of all the parts of the apparatus are known, surface area measurements can begin with an adsorbate. First, helium must be completely removed from the system and then stopcock A can be closed and either nitrogen or carbon dioxide admitted to the system from the reservoirs. The total volume of the adsorbate is determined as with helium previously. Then, with a constant temperature bath surrounding the sample (77 K for N_2, and first 298 and then 195 K for CO_2) and with the mercury level in the burette system at line six, one opens stopcock A and allows the system to equilibrate for one-half hour. After the equilibration time, one measures the pressure, P, and the temperature of the burette bulbs, T, and the constant temperature bath; repeating this procedure the level of the mercury is moved to the next line, decreasing the volume in the system, and allowed to equlibrate. In general this procedure is repeated for at least three points or until the relative pressure is around 0.25 to 0.30. To calculate the volume adsorbed, V, at each pressure use:

$$V = V_T - [\, V_R + V_A(1 + \alpha P/760)]$$

Where:

V_T = the total volume of adsorbate taken

V_R = the volume of adsorbate in the burette system, equal to $V_f P/T$

V_A = the volume of adsorbate in the adsorption bulb, equal to $f_B P$

and $(1 + \alpha P/760)$ is a correction factor for nonideality where α is a constant dependent on the adsorbate and temperature used. Values for α have been reported by Emmett (20). For the surface area, one plots the necessary data using either the BET or D-P equation to arrive at V_m, and then equation (5) is used as previously described.

Thermal Conductivity Apparatus (TCA). The apparatus used is the Quantasorb surface area analyzer manufactured by the Quantachrome Corporation. The method was developed by Nelsen and Eggertsen (27) and involves measuring the change in thermal conductivity of nitrogen/helium flows due to adsorption or desorption. Operation of the equipment is straightforward and there is no need to calculate dead space as in the volumetric apparatus. The sample is placed in a U-tube and degassed in a stream of nitrogen at 130°C for at least two hours. The sample, at room temperature, is then subjected to a stream of nitrogen-helium of known composition. The flow of gases is passed through the reference arm before entering the sample cell and then enters the measuring arm of the thermal conductivity cell. When a steady baseline is attained, the liquid nitrogen bath can be applied to the sample cell. Adsorption of nitrogen from the

gas stream occurs and causes a change in its composition which is detected by the thermal conductivity cell. The result is a peak which returns to the baseline once steady state flow conditions are reestablished. Since the diffusion of nitrogen into coals is slow, a half hour equilibration time is used for each partial pressure. The liquid nitrogen bath is then removed and the sample cell is warmed quickly to room temperature with the aid of a water bath. This procedure helps avoid any thermal diffusion problems. A peak representing the desorption of nitrogen is obtained, that is nearly equal to the adsorption peak. The desorption peak is used for calibration because there is less tailing then in the adsorption peak, especially with coal samples. The apparatus integrates the area under the peak and this is calibrated by injecting a known volume of nitrogen into the flow so that the calibration peak height is within 10-20% of the desorption peak height. The volume of nitrogen adsorbed at that relative pressure is then:

$$V = A_{des} \cdot \frac{V_{cal}}{A_{cal}}$$

Where:

V = volume of nitrogen adsorbed

A_{des} = integrated area under the desorption peak

V_{cal} = volume of nitrogen used in calibration

A_{cal} = integrated area under the calibration peak

The measurements are then repeated at two other relative

pressures and the surface area is calculated as previously described.

Nelsen and Eggertsen (12) measured nitrogen adsorption of several adsorbents. The surface area obtained from the thermal conductivity method agreed within 4% for silica-alumina craking catalysts to that obtained from a volumetric apparatus. Several others have also used this newer technique (TCA) with comparable results and I have also compared three coal samples in Table 1. In a few cases, only one point was taken at a relative pressure of 0.10. That volume adsorbed is assumed to be equal to V_m because it is located at the "knee" of the isotherm or point B as pointed out by Brunauer, Emmett and Teller (19).

Since carbon dioxide is adsorbed at room temperatures, the same technique can not be used. If one uses a 150°C bath to desorb carbon dioxide and then applies a 25°C water bath around the cell, values are close to that obtained with the volumetric apparatus but still differ some (-14%) due to small amounts of CO_2 still adsorbed at 150°C. Therefore, the surface area values for CO_2 obtained from the thermal apparatus were smaller then those obtained on the volumetric apparatus. The same can be said with desorbing at 150°C and then applying a -78°C bath around the cell. Therfore, it was necessary to equilibrate the sample to a preset flow of carbon dioxide-helium at 25°C and then apply a -78°C bath. Since the CO_2 25°C adsorption runs were all run on the vol-

umetric apparatus, a correction could be applied to the thermal apparatus. At each absolute pressure of carbon dioxide on the -78°C run the amount of CO_2 adsorbed at 25°C (from the volumetric apparatus) was added to the volume adsorbed going from 25° to -78°C; therefore, the total volume of carbon dioxide adsorbed is known. Calculations can now be done as previously described to arrive at the surface area of the adsorbent due to carbon dioxide adsorption at -78°C.

All CO_2 adsorptions at 25°C are performed on the volumetric apparatus and CO_2 adsorptions at -78°C are performed on one apparatus or the other; the volumetric apparatus is preferred. The nitrogen adsorptions at -196°C are performed on the thermal apparatus. See Tables I and II for a comparison of methods for nitrogen and carbon dioxide, respectively.

Microwave Apparatus. The apparatus used for microwave discharge was a Raytheon microwave generator (2450 MHz) coupled to an air-cooled Ophthos coaxial cavity (loaned by Dr. C. Gatz). The cavity was attached to a Pyrex-glass line shown in Figure 2 and consists of:

- a flow meter F
- a Hg bubbler for over pressure B
- a Hg manometer M
- the microwave cavity C

Furnaces. The furnace used for heating the coal sam-

TABLE I

COMPARISION OF THERMAL/VOLUMETRIC METHODS FOR DETERMINING THE SURFACE AREA WITH N_2 OF COALS

	Surface area m^2g^{-1}	
Sample[a]	Thermal	Volumetric
1	28.8 (3 pts.)	29.2
2	17.6 (1 pt.)	17.1
3	< 1 (1 pt.)	< 1

[a]1- PSOC 138, 400°C, 4 hours, O_2:N_2, 5%:95%

2- PSOC 371, 400°C, 4 hours, O_2:N_2, 5%:95%, prepared by S.Leon Arredondo (17)

3- PSOC 371, 350°C, 4 hours, N_2

TABLE II

COMPARISION OF THERMAL/VOLUMETRIC METHODS FOR DETERMINING THE SURFACE AREA WITH CO_2 (195 K) OF COALS

	Surface area $m^2 g^{-1}$	
Sample[a]	Thermal	Volumetric
1	22	20
2	231	239
3	29	27

[a]1- PSOC 371, 375°C, 4 hours, N_2

2- PSOC 138, 400°C, 4 hours, O_2:N_2, 5%:95%

3- PSOC 371, 400°C, 4 hours, N_2

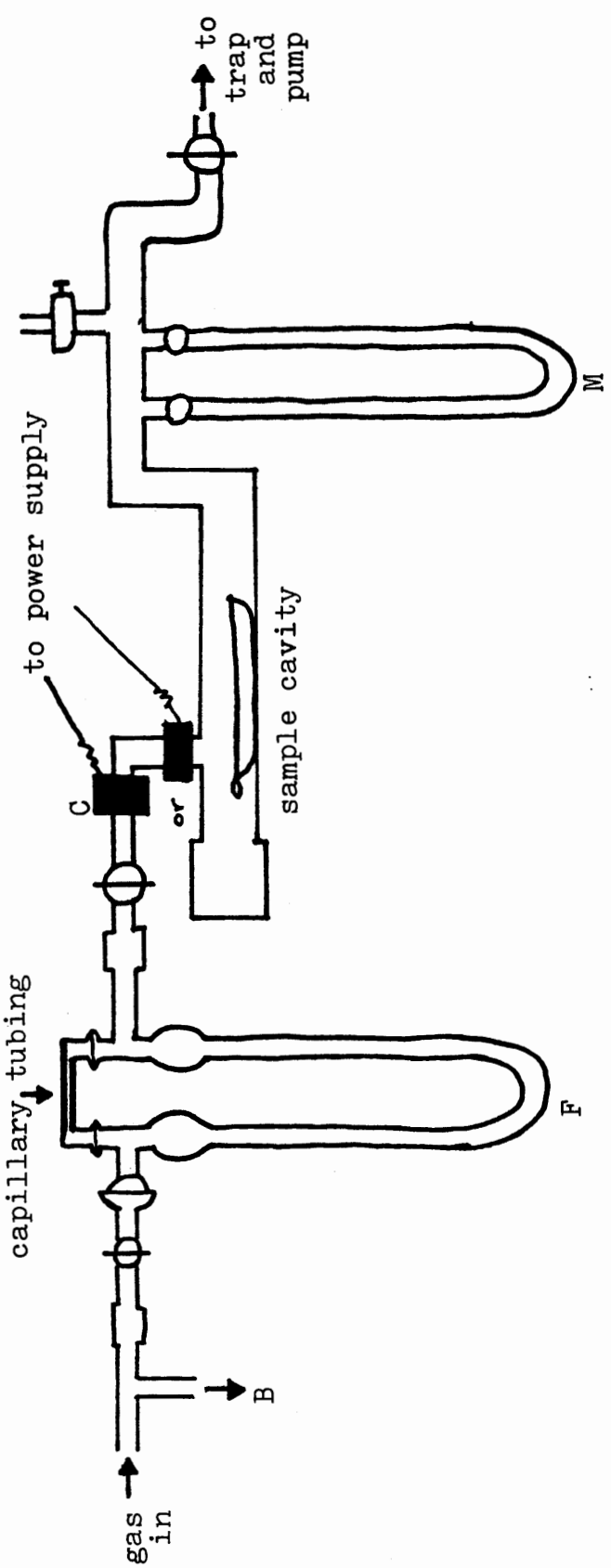

Figure 2. Diagram of microwave apparatus.

ples in a flow of gas was a horizontal tube furnace manufactured by Lucifer Furnaces, Inc., Warrington, PA, and had a maximum temperature of 1000°C. The tube inside the furnace was made of quartz with a 2.5 cm inner diameter. For heating the coal samples, treated with chromyl chloride, a vertical cup furnace was used which was manufactured by Jelrus Technical Products Corp. of New York and has a maximum temperature of 1100°C.

Auxillary Equipment. A quartz boat was used for the heat treatments of the coals in the horizontal furnace. It measured 15.5 cm long by 2.0 cm wide by 1.5 cm deep. Plain end flow meters used were manufactured by Manostat and RGI and were calibrated via the bubble flow method. Temperaturs in the furnace were measured with a chromel-alumel thermocouple and the constant temperature baths, room temperature and below, with copper constantan. Both were connected to a Fluke digital multimeter model 8810A manufactured by The John Fluke Mfg. Co.

Chemicals. Helium, hydrogen, nitrogen and oxygen gases (chemically pure grade) were obtained from Airco. The carbon dioxide gas was from Industrial Air Products Co., research grade. Absolute methanol (J.T. Baker) was used with dry ice in the 195 K bath. The pyridine used for solvent extraction was manufactured by Mallinckrodt (AR grade) and the chromyl chloride used was obtained from Pfaltz and Bauer, Inc.

Coals. The coals in this study are provided by Pennsylvania State University Coal Research Section and are PSOC 379, PSOC 371 and PSOC 190. The analysis of the coal samples are provided in Tables III to V, respectively. All samples are sieved to -20+42 Tyler mesh size before use and stored in screw top jars.

Pretreatments

Nitrogen-atmosphere, heating to 600°C. The coal was spread evenly in the quartz boat and then placed in the horizontal tube furnace. Sample sizes were about 5 grams for heating up to 500°C and about 3 grams for heating over 500°C. A flow of nitrogen, at 100 cc/min., was placed over the sample and after 15 minutes, heating began. The temperature was raised 10°C/minute to the desired temperature and was maintained for 4 hours (± 2°C). After that time, the heat was turned off and the sample was allowed to cool in the stream of nitrogen. When it was at room remperature, the sample was weighed and stored in a screw-cap sample bottle.

Oxygen-Nitrogen atmosphere, heating to 450°C. About 5 grams of coal was used and again spread uniformly in the quartz boat and placed in the horizontal tube furnace. A flow of oxygen-nitrogen, 5%:95% by volume, at 100 cc/min. was passed over the sample and after 15 minutes heating commenced. Again, the temperature was raised 10°C/min. and the desired temperature was maintained for 4 hours (± 2°C). After the heating period, the oxygen was turned off, and the

TABLE III

PROXIMATE AND ULTIMATE ANALYSIS OF PSOC-379

Proximate Analysis	As Rec'd	Dry	DAF*
% Moisture	1.62		
% Ash	15.80	16.06	
% Volatile	8.71	8.85	10.54
% Fixed carbon	73.87	75.09	89.46

Ultimate Analysis	As Rec'd	Dry	DAF*
% Ash	15.80	16.06	
% Carbon	75.22	76.46	91.09
% Hydrogen	3.22**	3.27	3.90
% Nitrogen	0.89	0.90	1.07
% Total sulfur	0.50	0.51	0.61
% Oxygen (diff)	2.75**	2.80	3.34

* Dry Ash Free

** excludes moisture

TABLE IV

PROXIMATE AND ULTIMATE ANALYSIS OF PSOC-371

Proximate Analysis	As Rec'd	Dry	DAF*
% Moisture	1.14		
% Ash	16.54	16.73	
% Volatile	30.39	30.74	36.92
% Fixed Carbon	51.93	52.53	63.08

Ultimate Analysis	As Rec'd	Dry	DAF*
% Ash	16.54	16.73	
% Carbon	69.82	70.63	84.82
% Hydrogen	4.53**	4.58	5.50
% Nitrogen	1.18	1.19	1.43
% Total sulfur	1.02	1.03	1.24
% Oxygen (diff)	5.77**	5.84	7.01

*Dry Ash Free

** excludes moisture

TABLE V

PROXIMATE AND ULTIMATE ANALYSIS OF PSOC-190

Proximate Analysis	As Rec'd	Dry	DAF*
% Moisture	16.14		
% Ash	7.12	8.49	
% Volatile	29.10	34.70	37.92
% Fixed carbon	47.64	56.81	62.08

Ultimate Analysis	As Rec'd	Dry	DAF*
% Ash	7.12	8.49	
% Carbon	57.99	69.15	75.57
% Hydrogen	4.10**	4.89	5.34
% Nitrogen	0.84	1.00	1.09
% Total sulfur	2.56	3.05	3.33
% Oxygen (diff)	11.25**	13.42	14.67

* Dry Ash Free

** excludes moisture

sample allowed to cool to room temperature in a stream of nitrogen. The sample was then weighed and stored in a screw-cap sample bottle.

Pyridine extraction for PSOC 371 and PSOC 190. Into a weighed 100 ml round bottom flask, about 15 grams of coal and 70 milliliters of pyridine were added. The flask was stoppered and the mixture was left to stir at room temperature for 48 hours. The sample was then filtered and washed with pyridine. After this, it was placed in a vessel which was attached to the vaccuum line and pumped on at 125 $\pm$ 5°C until constant weight was achieved (approximately 8 hours).

Treatment of PSOC 371 and PSOC 190 with chromyl chloride. In a 100 ml Pyrex-glass reaction vessel about 5 grams of PSOC 371 or PSOC 190 was added and then 20 grams of CrO_2Cl_2 was vacuum distilled into the vessel. The vessel was warmed to room temperature and then heated at 100°C for 24 hours. The CrO_2Cl_2 was then pumped off through a cold trap attached to a vacuum line. After all visible traces of CrO_2Cl_2 were removed, the vessel was heated to 120°C until constant weight was achieved. The surface area of the coal sample was then measured. Heating to higher temperatures was executed by placing the coal sample in a quartz vessel, which was then inserted into the vertical cup furnace; surface area measurements were then taken after each heating as described later.

Hydrogen atom treatment. About one gram of coal was

placed in a quartz boat and then placed in the microwave apparatus, see Figure 2. The sample was then pumped down, and heated to the desired temperature and held there for about 20 minutes before hydrogen gas was added. The hydrogen flow was set at 50 cc/min., and after 2 minutes the microwave generator was started with a Tesla coil and the pressure of the system was recorded. The discharge was left to go for a set time, and then the power was turned off along with the hydrogen. The system was then left to cool to room temperature and to pump down for at least one hour.

To test for the presence of hydrogen atoms, powdered WO_3 was placed in the quartz boat and then into the sample cavity. The same procedures were used as above to start the discharge. Within a minute, the surface of the WO_3 turned blue, indicating the presence of hydrogen atoms.

Oxygen atom treatment. The same procedure described for the hydrogen atom treatment was used, except that Fe_2O_3 was placed at the end of the quartz boat to insure all active species of oxygen are deactivated.

CHAPTER III

RESULTS AND DISCUSSION

Volatile matter is released when coal is thermally heated thereby creating added porosity and surface area. This increase in surface area is created by enlarging existing pores or by exposing previously blocked pores. In addition to a loss of volatile matter, cross-links found in the coal structure can be broken, which causes a loss of porosity and surface area because of better alignment of the aromatic regions in the coal. Therefore, there is likely to be a maximum surface area over a certain temperature range.

Also, coking coals differ from the non-coking coals in that they go through a plastic stage around 400°C, which can also alter the surface properties of the coal. Heating in a stream of nitrogen is done first, since temperature changes the surface area of coals and its effect must be measured, and then oxidation with oxygen is studied. Other pretreatments which possibly could significantly alter the surface area include: extraction with pyridine before the heat and oxidation treatments and reactions with chromyl chloride and hydrogen and oxygen atoms.

Finally, it was observed that the surface area of treated coals varied with time, at ambient conditions; this

phenomenon was studied.

Effect of heating in a nitrogen atmosphere on the surface area of coal. The method is described in the experimental section and the results follow.

For PSOC 371 (hvAb, caking coal), the temperature of treatment, weight loss (%) and the surface areas, as measured by N_2 (77K) and CO_2 (298 and 195K), are presented in Table VI. The nitrogen isotherms at 77K are in Figure 3 and the carbon dioxide isotherms are in Figures 4 and 5. The work is a review of S. Leon Arredondo (17) and compares well with his results except for the 600°C treatment. It is observed that relatively little change in the surface area, as measured by N_2 (77K), occurred by heating up to 500°C, whereas the surface area, as measured by CO_2 (298K), increases from 90 to 304 m^2g^{-1}. This is accompanied by a 22.4% weight loss at 500°C. The increase in the surface area, as measured by CO_2 (298K), could be due to unblocking pores or to the formation of new pores, however no pores in the range of 0.5 nm or larger are formed since the surface area, as measured by N_2 (77K), remained small. When the sample is heated at 600°C the surface area, as measured by N_2 (77K), became 10 m^2g^{-1} and the surface area, as measured by CO_2 (298K), is 383 m^2g^{-1}. At this temperature there is an increase of both large and small pores. Since PSOC 371 is a caking coal it has tendencies to agglomerate, and this is observed visually after heating at 400°, 500° and 600°C;

TABLE VI

EFFECT OF HEATING IN AN INERT ATMOSPHERE ON THE SURFACE AREA OF PSOC 371

Temperature of treatment (°C)	wt loss (%)	Surface area (m^2g^{-1}) N_2 (77K) BET	CO_2(195K) D-P/BET	CO_2(298K) D-P
raw	----	1.8	16/ 12.5	90
350	4.6	< 1	31/ 21	118
375	8.2	< 1	31/ 22	127
400	13.0	< 1	41/ 27	147
500	22.4	2.4	316/233	304
600	24.9	10	--/ 206	383

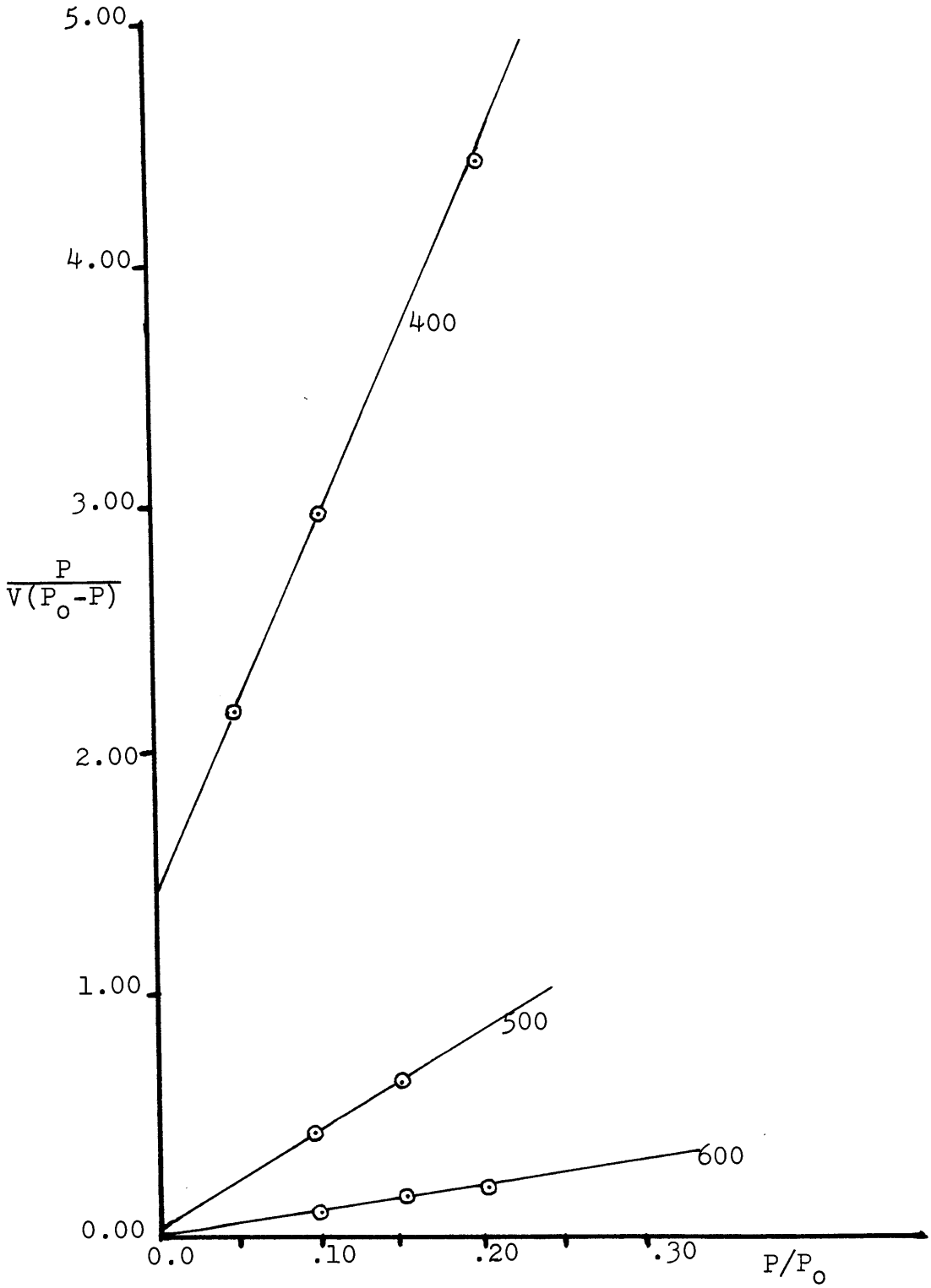

Figure 3. BET nitrogen isotherms at 77 K. Temperature treatment (°C) in nitrogen (PSOC 371).

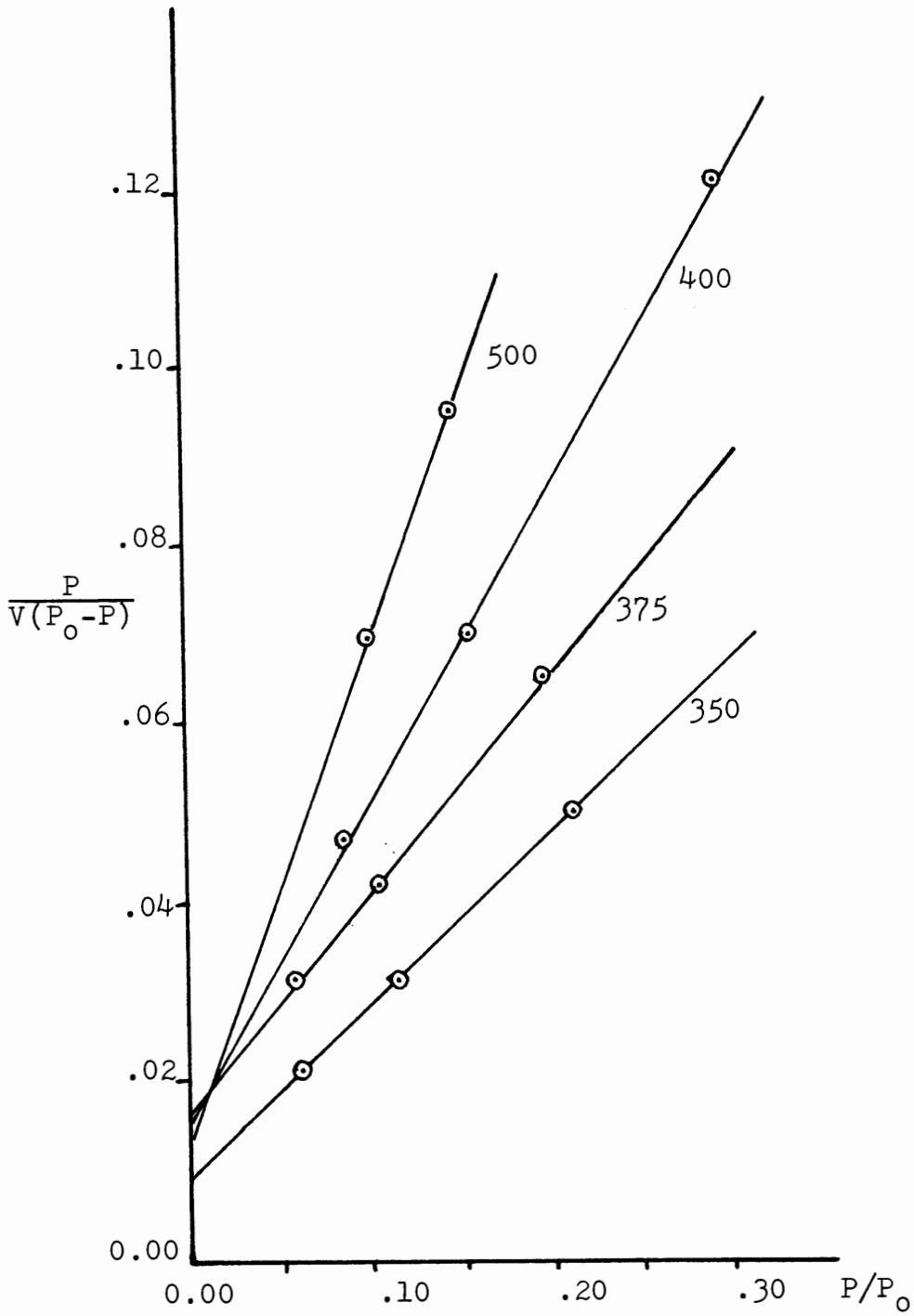

Figure 4. BET carbon dioxide isotherms at 195 K. Temperature treatment (^{o}C) in nitrogen (PSOC 371).

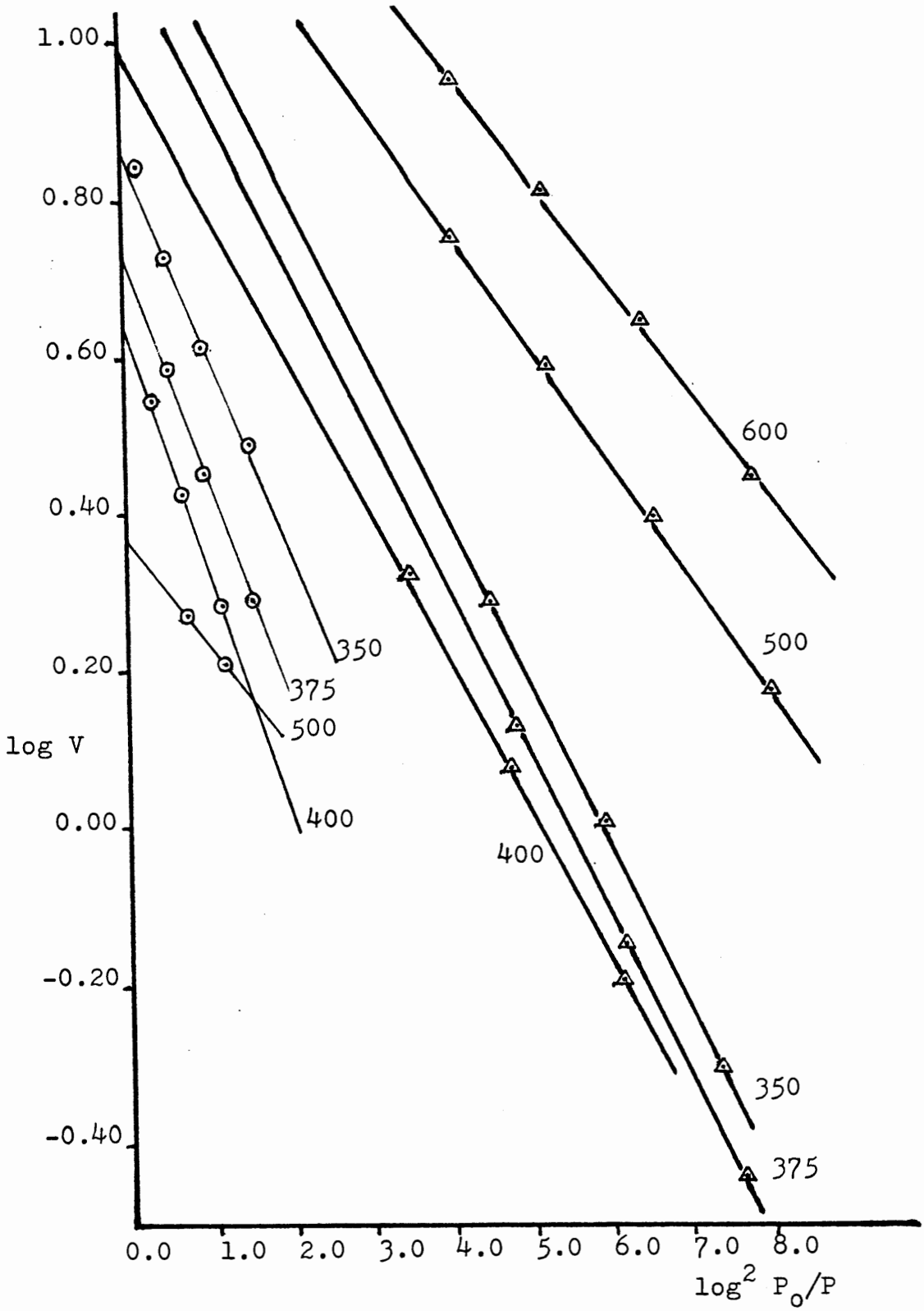

Figure 5. Dubinin-Polanyi carbon dioxide isotherms at 298 K (▲) and 195 K (⊙). Temperature treatment (^{o}C) in nitrogen (PSOC 371).

however, it is well know that preoxidation of caking coals prevents agglomeration (9).

The heat treatment data for PSOC 379 (semi-anthracite) are found in Table VII. The B.E.T. and D-P plots are in Figures 6, 7 and 8. The surface area, as measured by N_2 (77K), changed little over the temperature range of 375° to 600°C, the values being 2.1 to 4.8 m^2g^{-1}, respectively. There is also relatively little weight loss, 5.6% at 600°C, due to the low percentage of volatile matter in the coal. The surface area, as measured by CO_2 (298K), changed little up to 400°C, but at 500°C increased to 356 m^2g^{-1} and at 600°C is 420 m^2g^{-1}, compared to 253 m^2g^{-1} for the raw coal. Again heating in an inert atmosphere does little to increase large pores but does increase the smaller pores.

Table VIII shows the effects of heating in nitrogen on PSOC 190 (hvCb); included are the weight loss (%) and the surface areas, as measured by N_2 (77K) and CO_2 (298 and 195K). Figures 9 and 10 show the B.E.T. and D-P plots, respectively. As can be seen from Table VIII the surface area, as measured by N_2 (77K), is initially high, 29 m^2g^{-1}; subsequent heating at 375°C and 400°C decreased the surface area to 5.2 and 4.6 m^2g^{-1}, respectively. This could be the result of blockage or collapse of pores larger then 0.5 nm from the release of volatile matter. The surface area, as measured by CO_2 (298K), for these same temperatures increased from the raw value of 168 m^2g^{-1} to 222 and 289

TABLE VII

EFFECT OF HEATING IN AN INERT ATMOSPHERE ON THE SURFACE AREA OF PSOC 379

Temperature of treatment (°C)	wt loss (%)	Surface area (m^2g^{-1}) N_2(77K) BET	CO_2(195K) D-P/BET	CO_2(298K) D-P
raw	---	2.0	52/ 36	253
375	2.0	2.1	71/ 51	258
400	2.1	2.5	67/ 48	252
500	4.5	3.6	114/ 82	356
600	5.6	4.8	185/138	420

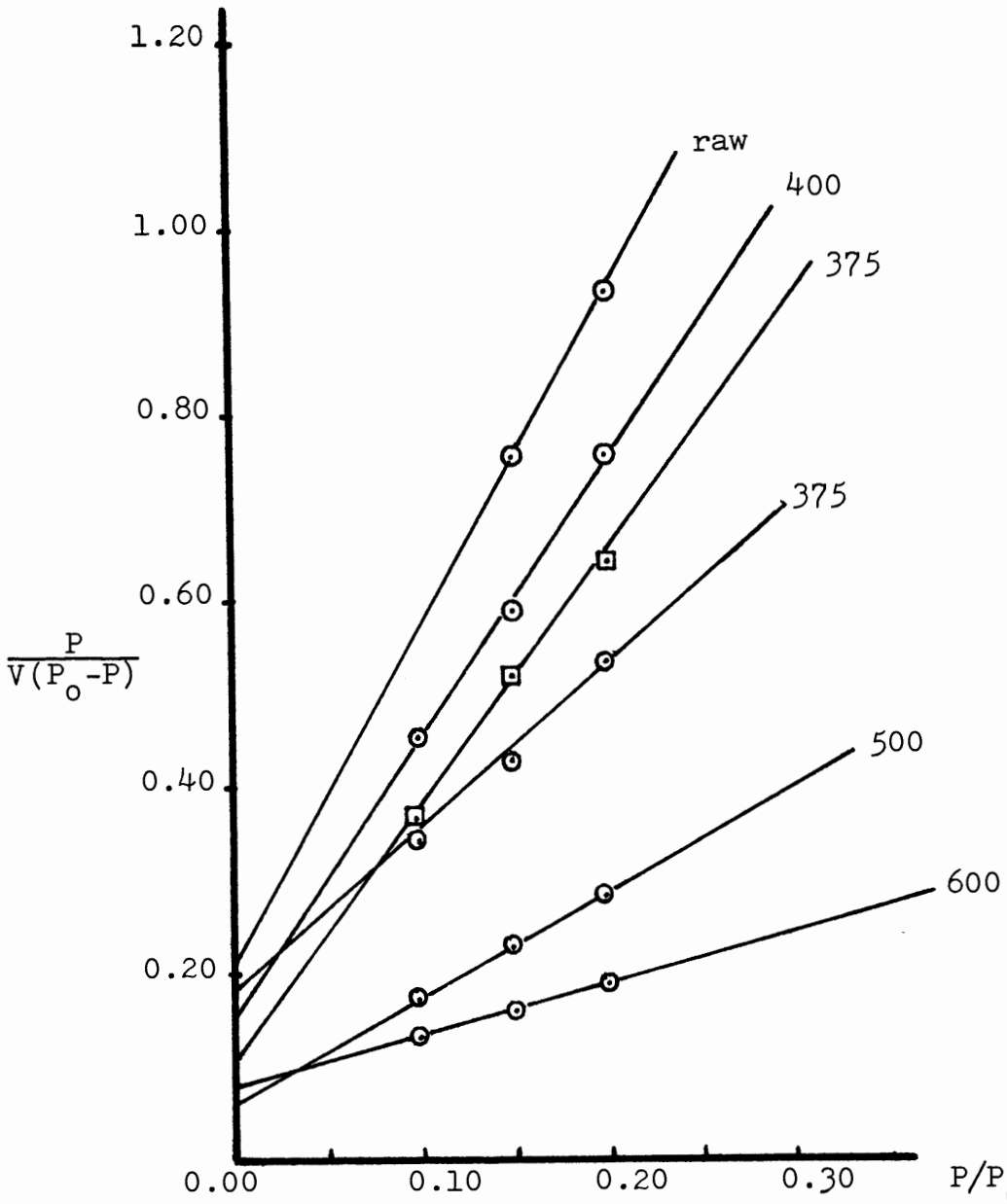

Figure 6. BET nitrogen isotherms at 77 K (⊡) and carbon dioxide at 195 K (⊙). Temperature treatment (^{o}C) in nitrogen (PSOC 379).

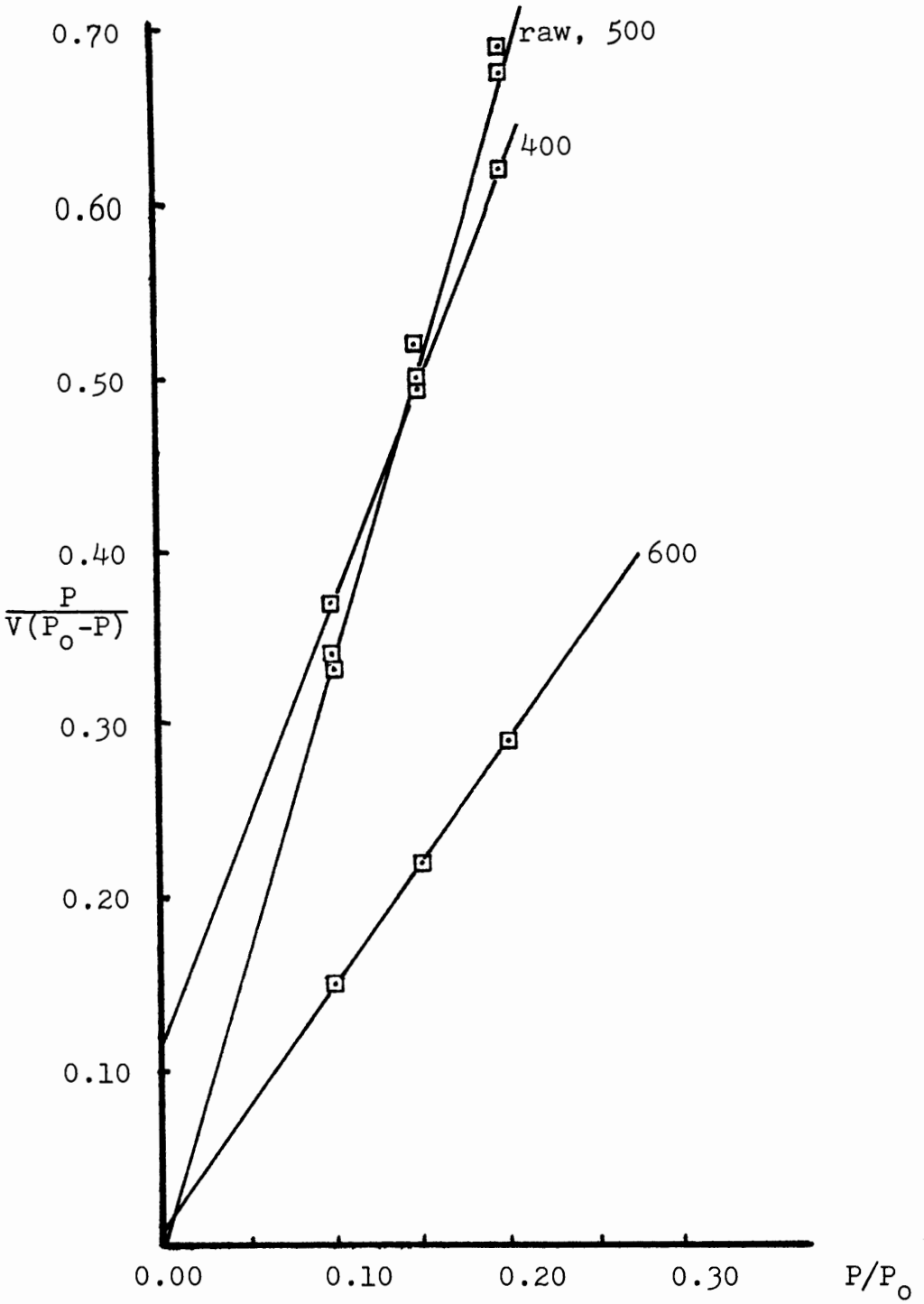

Figure 7. BET nitrogen isotherm at 77 K. Temperature treatment (^{o}C) in nitrogen (PSOC 379).

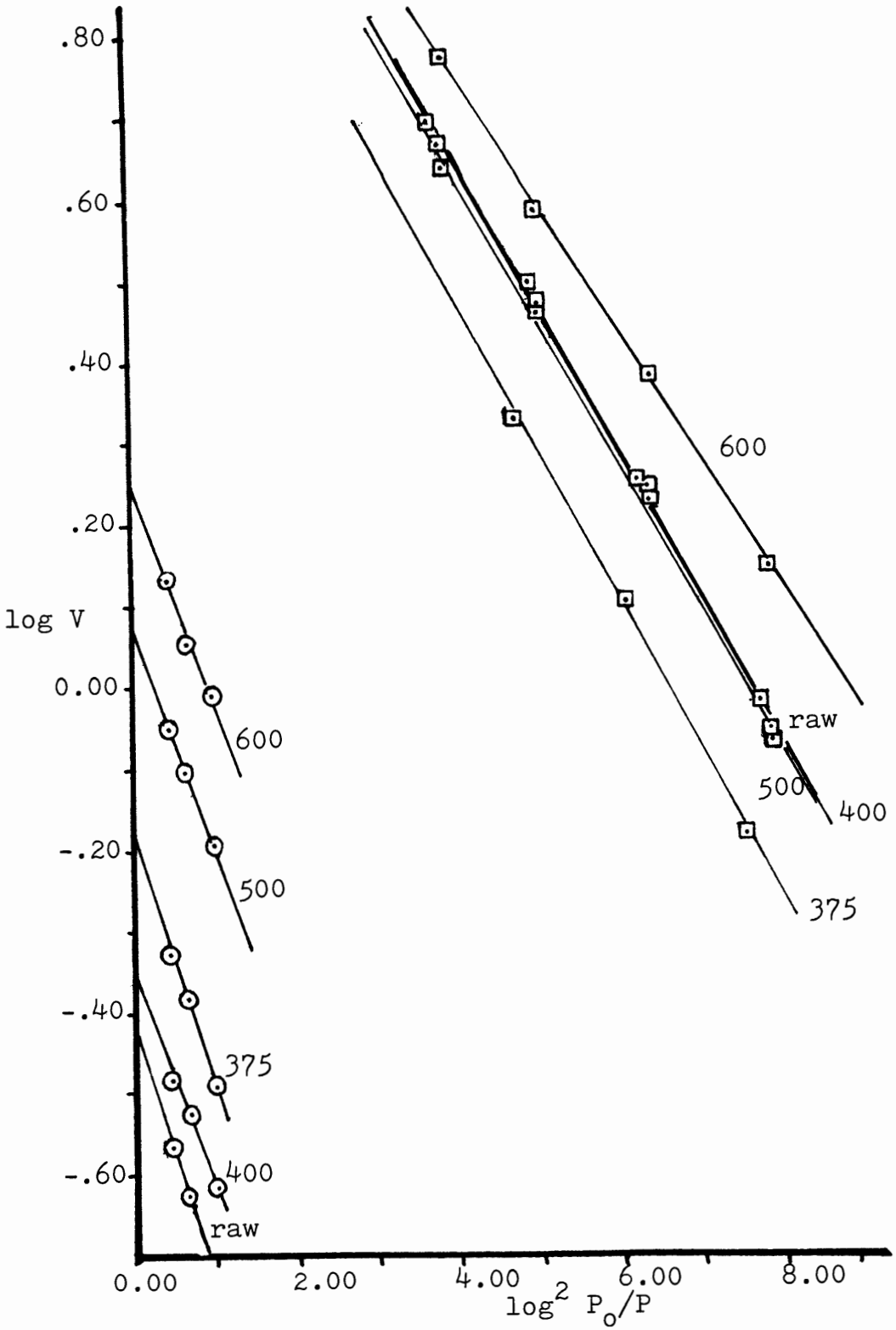

Figure 8. Dubinin-Polanyi carbon dioxide isotherms at 298 K (⊡) and 195 K (⊙). Temperature treatment (^{o}C) in nitrogen (PSOC 379).

TABLE VIII

EFFECT OF HEATING IN AN INERT ATMOSPHERE ON THE SURFACE AREA OF PSOC 190

Temperature of treatment (°C)	wt loss(%)	Surface area (m^2g^{-1}) N_2(77K) BET	CO_2(195K) D-P/BET	CO_2(298K) D-P
raw	---	29	193/138	168
375	19.2	5.2	125/ 94	222
400	22.2	4.6	158/115	289
500	29.0	18	354/275	476
600	34.8	38	385/273	675

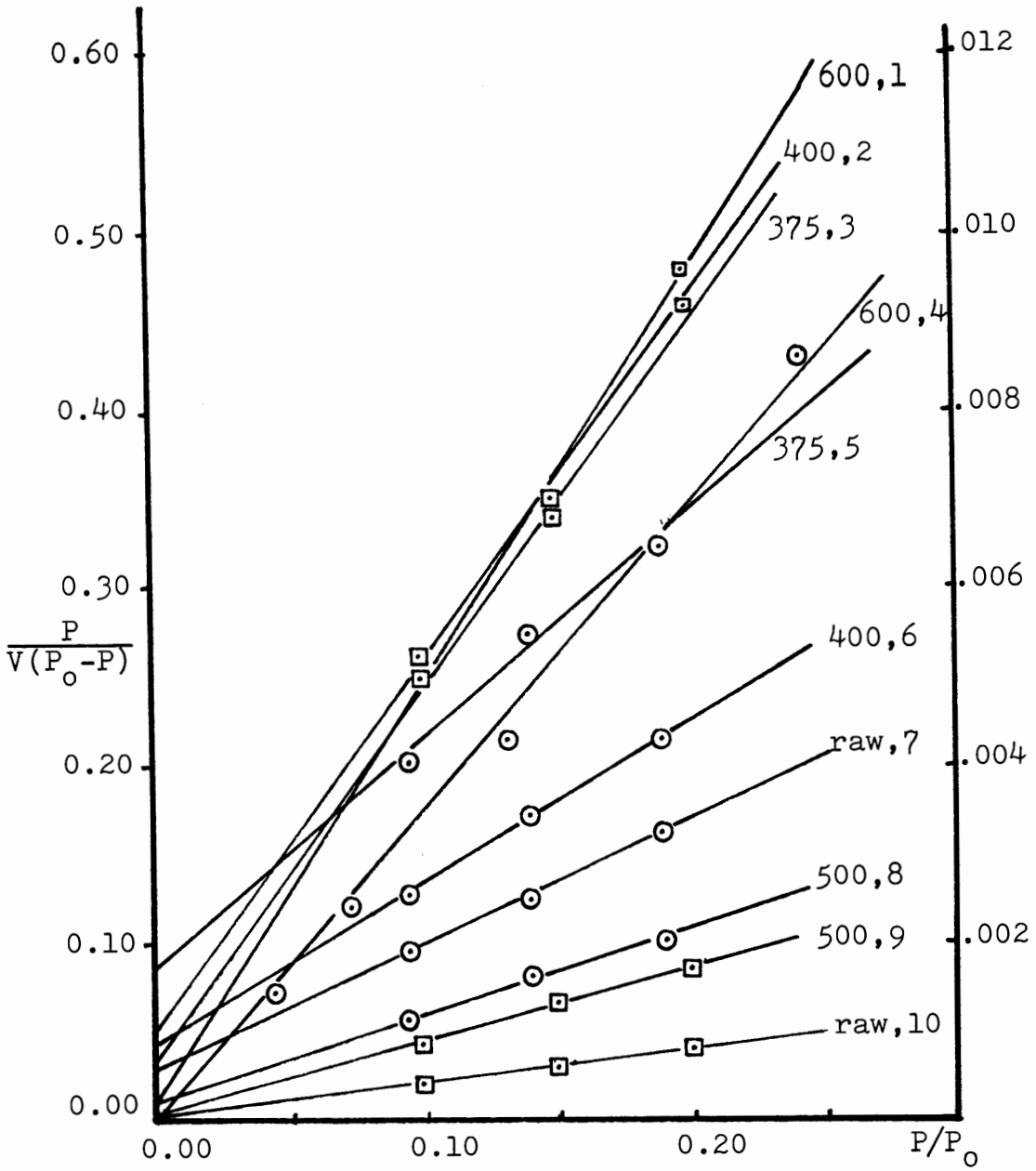

Figure 9. BET nitrogen isotherms at 77 K (⊡) and carbon dioxide at 195 K (⊙). Temperature treatment (^{o}C) in nitrogen (PSOC 190). Use the right-hand ordinate for line 4 and the left ordinate for all other lines.

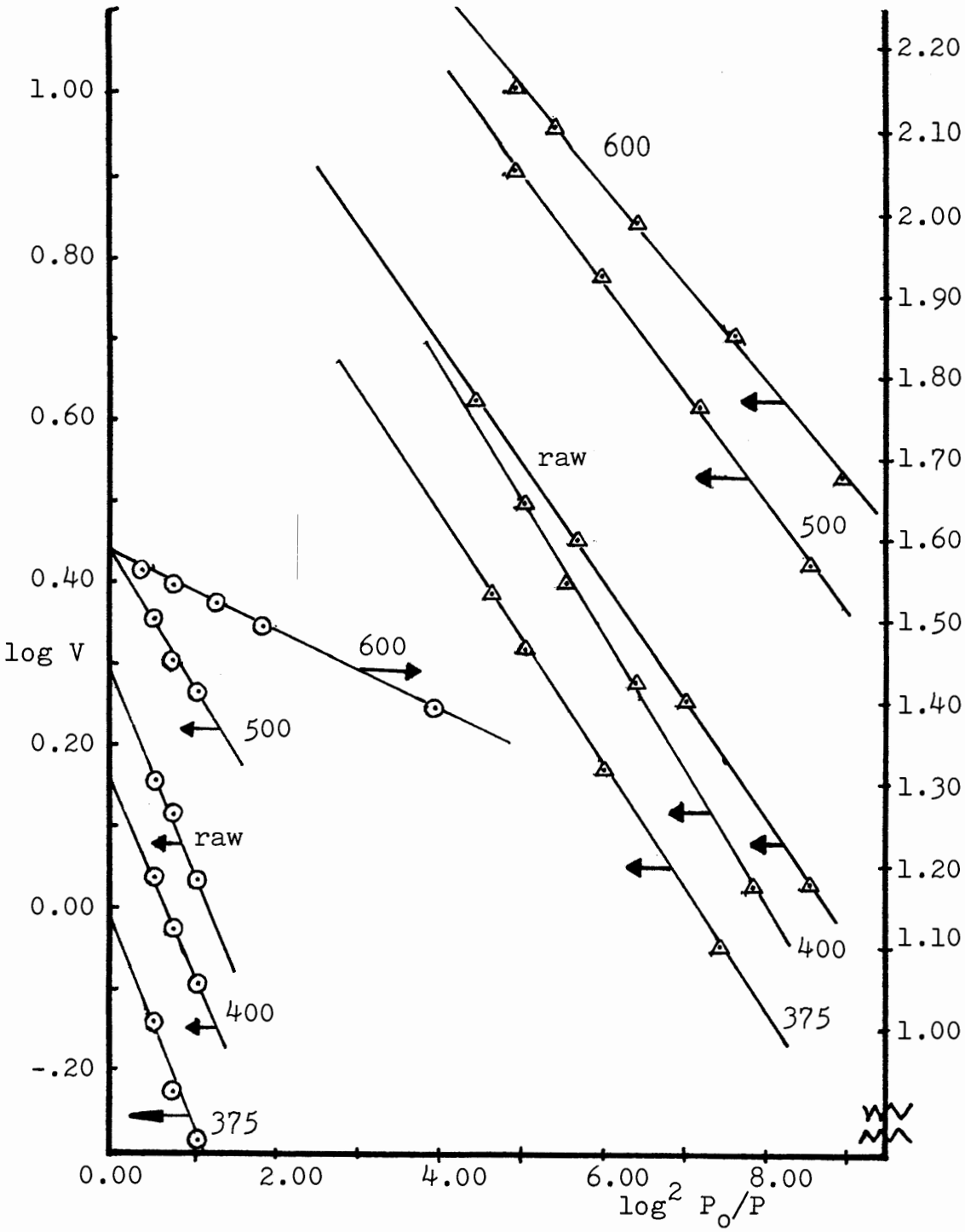

Figure 10. Dubinin-Polanyi carbon dioxide isotherms at 298 K (△) and 195 K (⊙). Temperature treatment (^{o}C) in nitrogen (PSOC 190).

m^2g^{-1}, respectively. PSOC 190 has a high percentage of volatile matter, higher then PSOC 371 or PSOC 379 (on a DAF basis), and this is seen in the weight loss upon heating. For example, at 400°C the weight loss is 22% for PSOC 190 but only 13.0 and 2.1% for PSOC 371 and PSOC 379, respectively. At 500°C the surface area, as measured by N_2(77K), is 18 m^2g^{-1} and at 600°C is 38 m^2g^{-1} (the raw coal has a value of 29 m^2g^{-1}). The weight loss is 29.0 and 34.8% at 500° and 600°C, respectively. There is probably some clearing of the pores by removing volatile matter or the formation of some new pores. The surface area, as measured by CO_2 (298K), continues to increase to 675 m^2g^{-1} at 600°C.

The preceding data for all three coal samples shows that heating up to 600°C in a stream of nitrogen does not significantly increase the surface area, as measured by N_2 (77K). It is also observed that the weight loss upon heating increased as the rank of the coal decreased; that is, the highest ranked of the three coals studied, PSOC 379, has the lowest percent weight loss and the lowest ranked coal, PSOC 190, has the highest percent weight loss, for the same temperature. This type of correlation has been observed before (9, 28) and is also indicative of the percent of volatile matter present in the coals on a dry ash free basis (see proximate analysis of the coals in the experimental section). The surface area, as measured by

CO_2 (298K), for the three coal samples studied over the temperature range 350° to 600°C increased and reached a maximum at 600°C. The increase in the surface area, as measured by N_2 (77K) and CO_2 (298K), would be due to the loss of volatile matter, dehydration and possibly due to structural changes upon heating.

Effect of oxygen pretreatment on the surface area of coals. The experimental method is described in the previous chapter and the results are discussed below.

It was reported previously (17) that the surface area for PSOC 371, as measured by N_2 (77K), was 52 m^2g^{-1} upon pretreatment in O_2/N_2 at 400°C and that it decreased at higher temperatures. The original sample heated at 300°C had a value of less then 1 m^2g^{-1}. The present work was extended to narrow the temperature range of 300-400°C by making measurements at 350°, 375° and 400°C (Table IX). The BET and D-P plots are in Figures 11 and 12, respectively.

The present results confirm that heating at 400°C produces the maximum surface area, as measured by N_2 (77K), but a value of 72 m^2g^{-1} is obtained not 52 m^2g^{-1}. However, the weight loss is also different, 14.7% compared to 9.7%, and might explain the difference in the surface area values. The surface area, as measured by CO_2 (298K), increased only 18 m^2g^{-1} from that previously reported (17).

The results for PSOC 379 are in Table X and the B.E.T. and D-P plots are in Figures 13 and 14, respectively. It

TABLE IX

EFFECT OF OXYGEN PRETREATMENT ON THE SURFACE AREA OF PSOC 371

Temperature of treatment (°C)	wt loss (%)	Surface area (m^2g^{-1}) N_2(77K) BET	CO_2(195K) D-P/BET	CO_2(298K) D-P
350	3.1	< 1	41/ 32	98
375	6.3	< 1	94/ 73	154
400	14.7	72	193/155	253

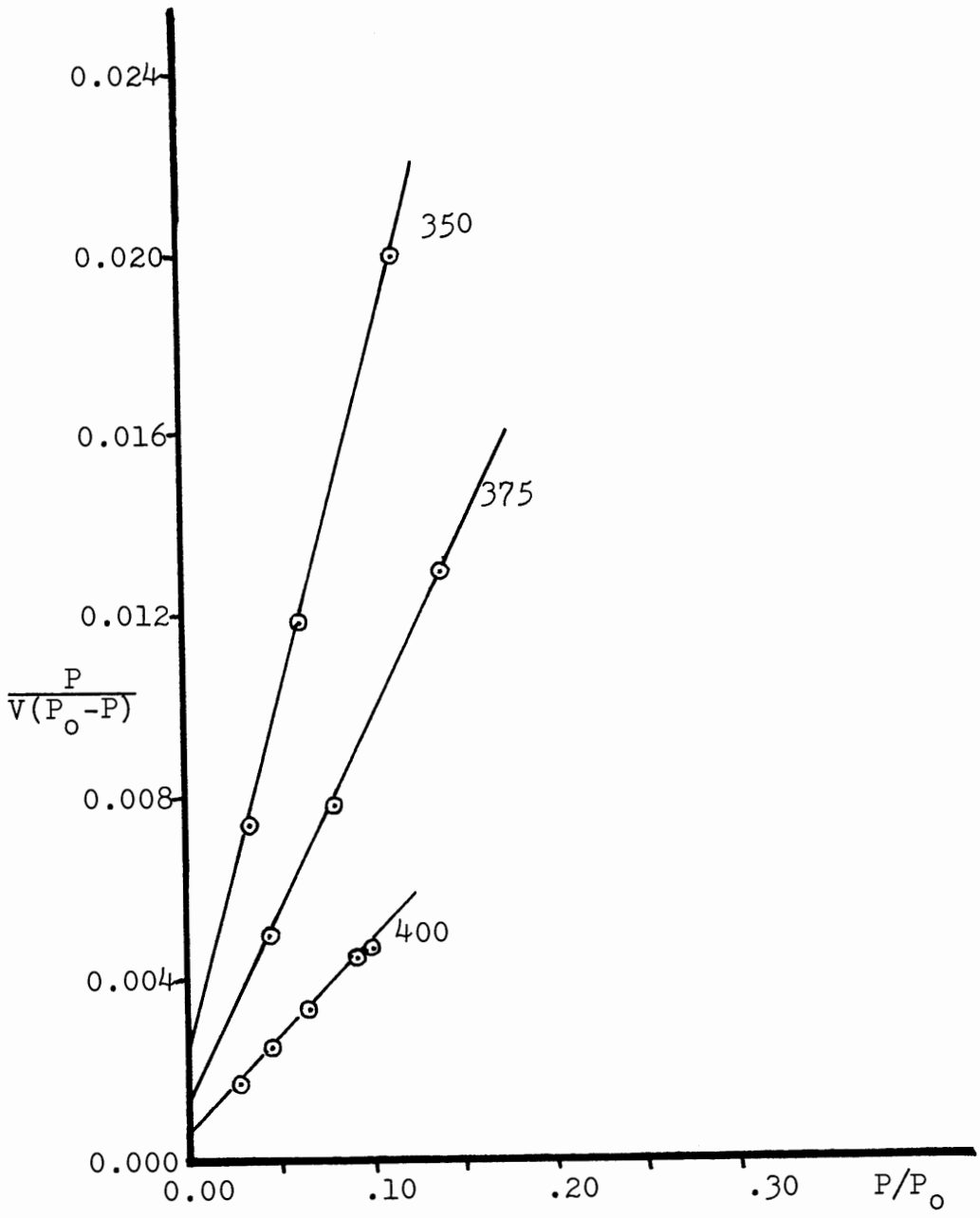

Figure 11. BET carbon dioxide isotherms at 195 K. Temperature treatment (^{o}C) in oxygen-nitrogen (PSOC 371).

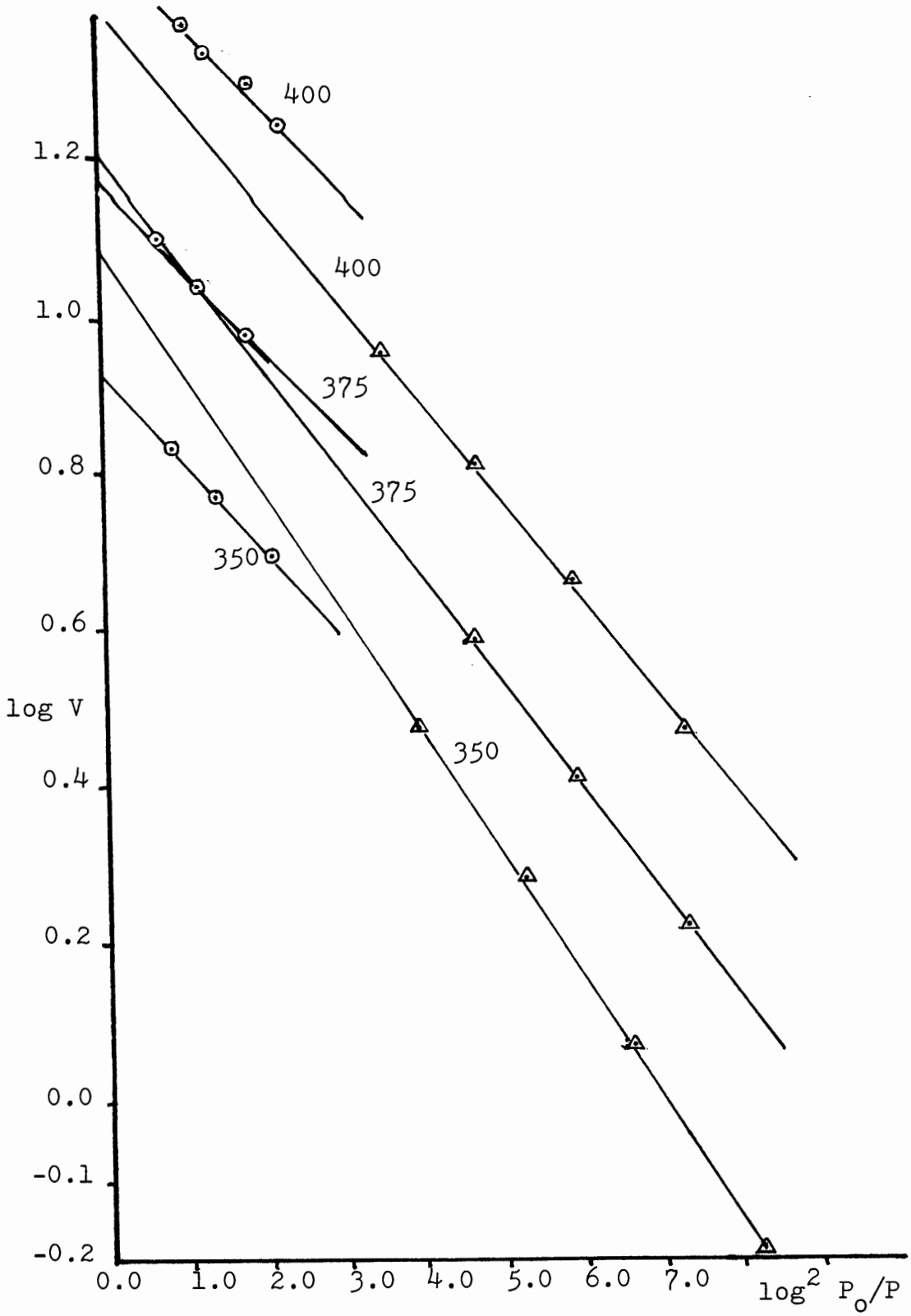

Figure 12. Dubinin-Polanyi carbon dioxide isotherms at 298 K (▲) and 195 K (⊙). Temperature treatment (^{o}C) in oxygen-nitrogen (PSOC 371).

TABLE X

EFFECT OF OXYGEN PRETREATMENT ON THE SURFACE AREA OF PSOC 379

Temperature of treatment (°C)	wt loss (%)	Surface area (m^2g^{-1}) N_2(77K) BET	CO_2 (195K) D-P/BET	CO_2(298K) D-P
375	1.6	5.7	85/ 63	226
400	2.2	17	126/ 92	287
425	3.7	49	217/109	257
450	5.6	120	225/170	307

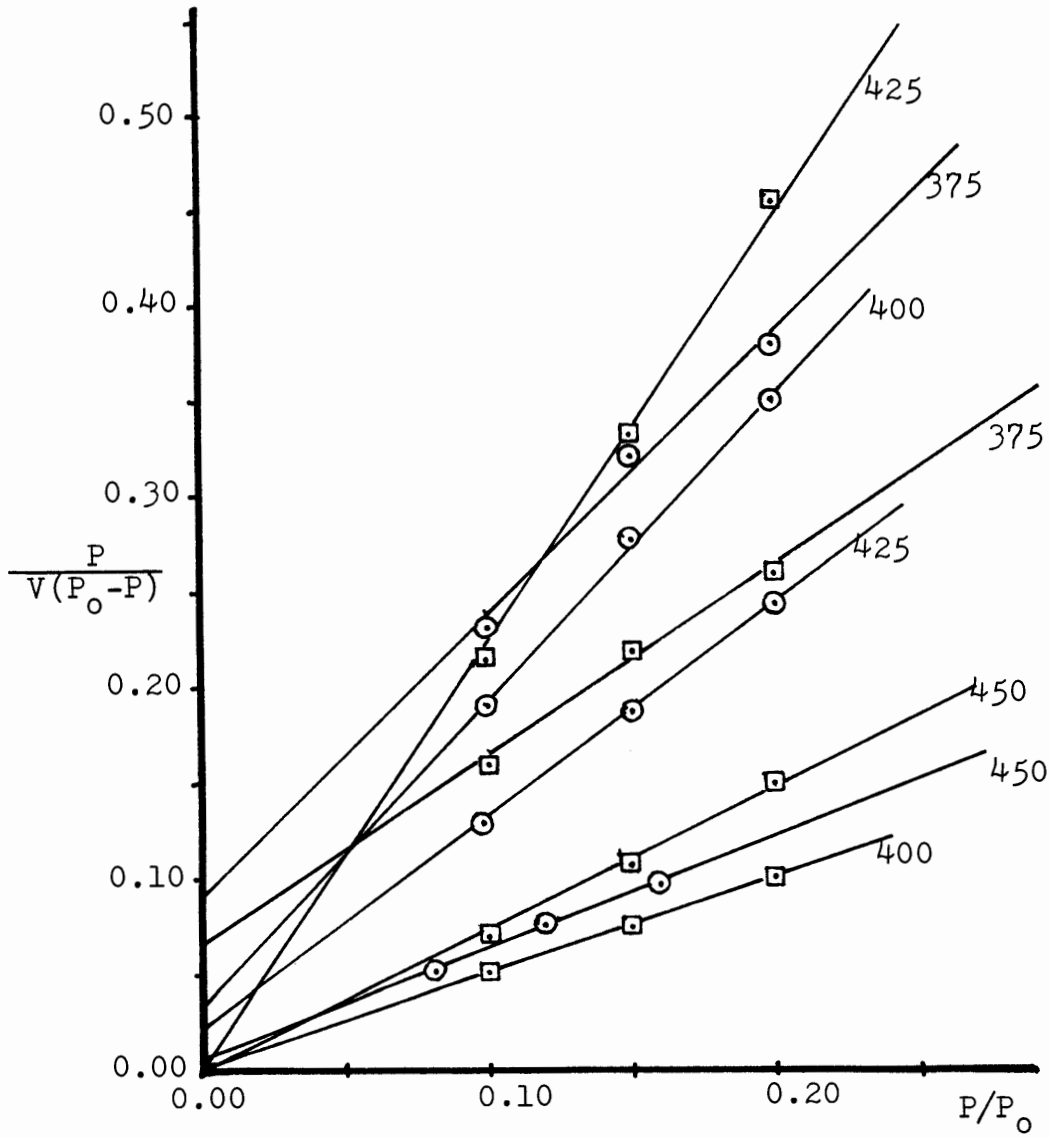

Figure 13. BET nitrogen isotherms at 77 K (⊡) and carbon dioxide at 195 K (⊙). Temperature treatment (^{o}C) in oxygen-nitrogen (PSOC 379).

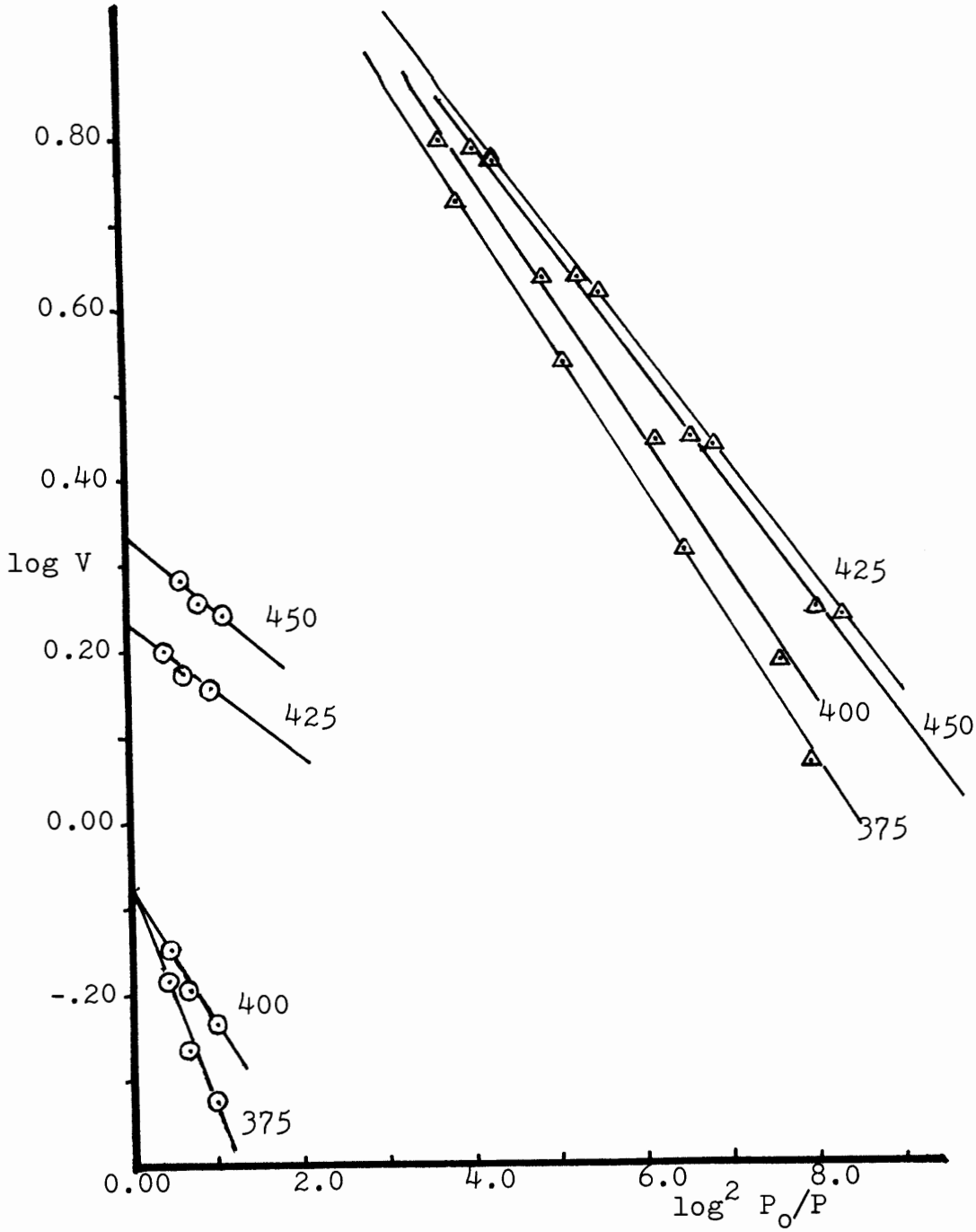

Figure 14. Dubinin-Polanyi carbon dioxide isotherms at 298 K (△) and 195 K (⊙). Temperature treatment (^{o}C) in oxygen-nitrogen (PSOC 379).

is observed that the surface area, as measured by N_2 (77K), from 375° to 450°C increased up to 450°C, 120 m^2g^{-1}, with relatively little weight loss, 5.6% at 450°C. The surface area, as measured by CO_2 (298K), also increased and has a value of 307 m^2g^{-1} at 450°C (the raw coal has a value of 226 m^2g^{-1}). At this temperature there is an increase in pores both larger and smaller then 0.5 nm.

The weight loss (%) and surface areas, as measured by N_2 (77K) and CO_2 (195 and 298K), at 350°, 375°, 400° and 425°C in 5%O_2:95%N_2 for PSOC 190 are presented in Table XI. The B.E.T. and D-P plots are in Figures 15 and 16, respectively. The weight loss ranges from 17.0 to 25.5% for the temperature range of 350° to 425°C, respectively. The surface area, as measured by N_2 (77K), at 350°C is only 19 m^2g^{-1}, compared to 29 m^2g^{-1} for the raw coal, but increased to 82 and 87 m^2g^{-1} at 375° and 400°C, respectively, and then dropped to 37 m^2g^{-1} at 425°C. This result could be due to an initial collapse or blockage of the pores larger then 0.5 nm at 350°C and then unblocking or creation of larger pores from smaller ones at 375° and 400°C and then a blocking or collapse of pores at 425°C. The surface area, as measured by CO_2 (298K), at 350°C is 299 m^2g^{-1} which then dropped to 278 m^2g^{-1} at 375°C but increased at 400°C and 425°C to 321 and 358 m^2g^{-1}, respectively.

The data presented above shows that the oxidation treatment of the three coals in 5%O_2:95%N_2 significantly

TABLE XI

EFFECT OF OXYGEN PRETREATMENT ON THE SURFACE AREA OF PSOC 190

Temperature of treatment (°C)	wt loss (%)	Surface area (m^2g^{-1}) N_2(77K) BET	CO_2(195) D-P/BET	CO_2(298K) D-P
350	17.0	19	240/179	299
375	21.8	82	249/181	278
400	26.7	87	275/214	321
425	25.5	37	269/204	358

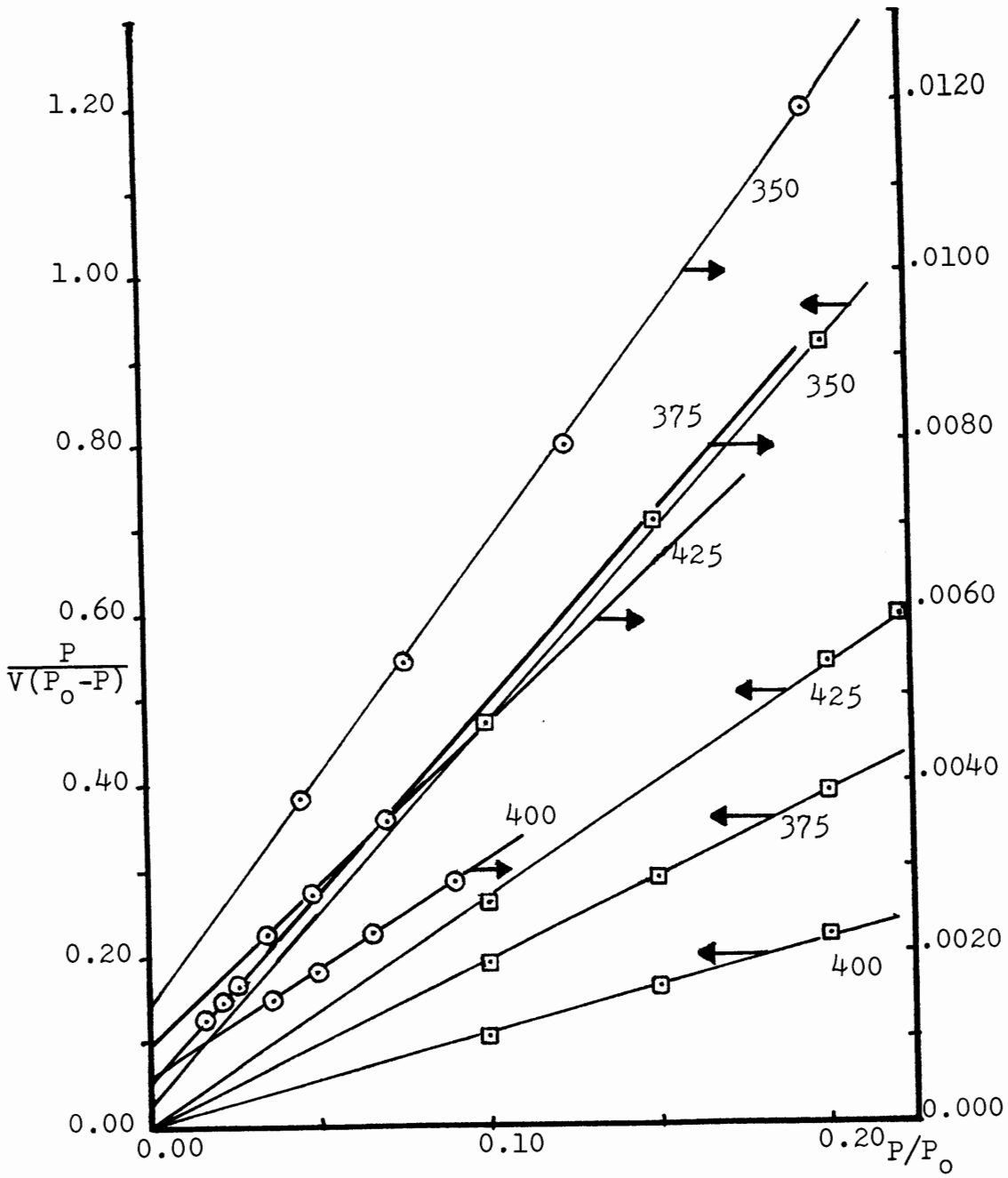

Figure 15. BET nitrogen isotherms at 77 K (⊡) and carbon dioxide at 195 K (⊙). Temperature treatment (^{o}C) in oxygen-nitrogen (PSOC 190).

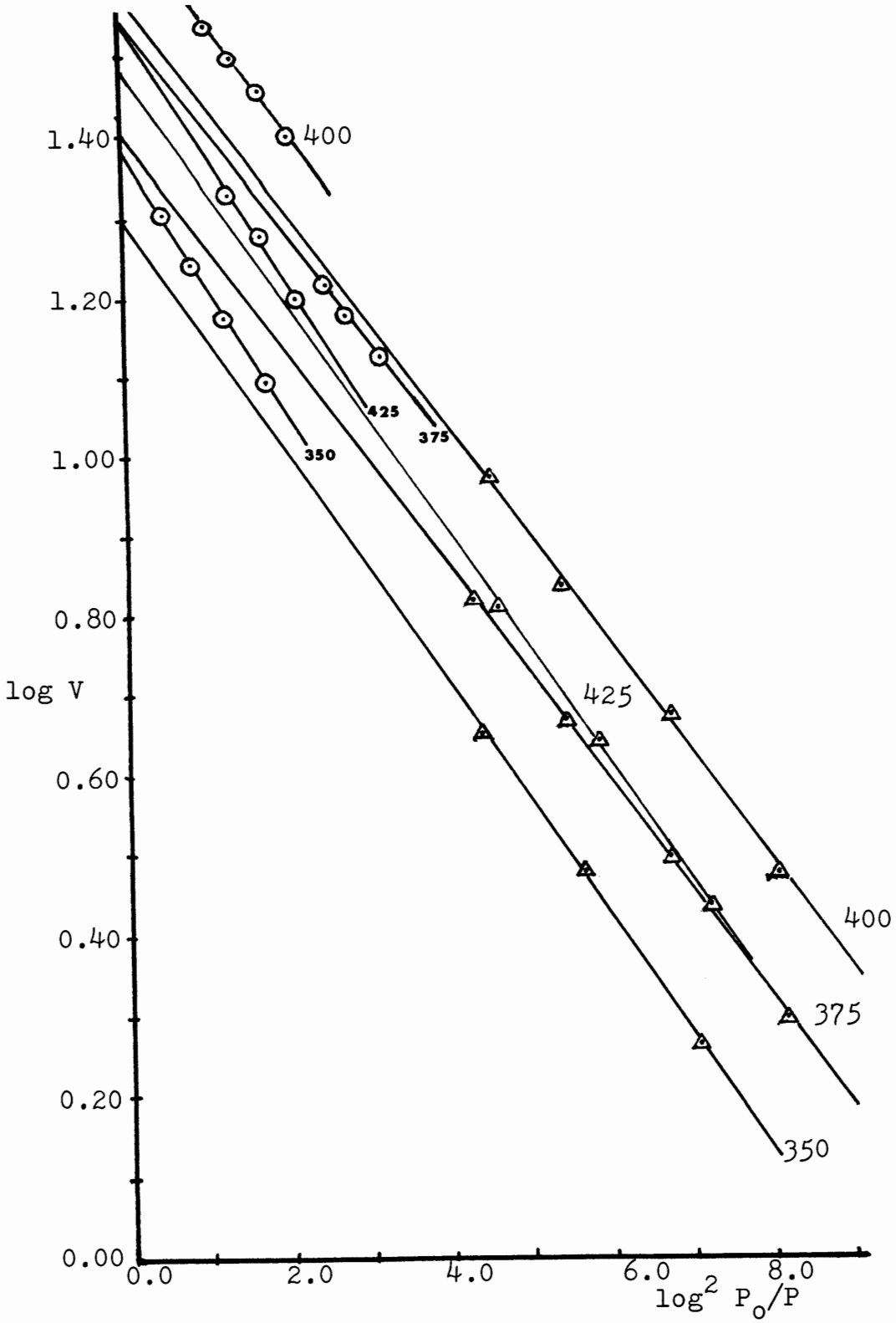

Figure 16. Dubinin-Polanyi carbon dioxide isotherms at 298 K (▲) and 195 K (⊙). Temperature treatment (^{o}C) in oxygen-nitrogen (PSOC 190).

increases the surface area, as measured by N_2 (77K), over the heat treatment in pure N_2 at temperatures around 400°C. The increase of these areas over the raw coals are 3, 40 and 60 times more for PSOC 190, PSOC 371 and PSOC 379, respectively. When compared to the heat treated coal, the increase is 19, > 80 and 40 for PSOC 190, PSOC 371 and PSOC 379, respectively. The surface area, as measured by CO_2 (298K), increased by 1.9, 2.8 and 1.2 times over the raw samples for PSOC 190, PSOC 371 and PSOC 379, respectively, but only by 1.1, 1.7 and 1.0 times over the heat treatment values, respectively. Therefore, a treatment of 5% O_2: 95% N_2 between 375° and 450°C is beneficial in opening the pores larger then 0.5 nm for a hvCb, hvAb and a semi-anthracite coal.

Effect of pyridine extraction with PSOC 371 and PSOC 190, and subsequent heat and oxidation treatments on the surface area. Solvent extraction can remove trapped molecules in coal; therefore , solvent extraction with pyridine at ambient temperature before the heat and oxidation treatments are attempted to increase the surface area, as measured by N_2 (77K). Table XII shows the weight loss (%) and the surface areas, as measured by N_2 (77K) and CO_2 (195 and 298K), after pyridine extraction and then after heat and oxidation treatments at 400°C for PSOC 371 and PSOC 190. The BET and D-P plots are in Figures 17-20.

From Table XII, pyridine extraction opens up pores

TABLE XII

EFFECTS OF PYRIDINE EXTRACTION AND SUBSEQUENT HEAT TREATMENTS ON THE SURFACE AREA FOR PSOC 371 AND PSOC 190

Coal	Treatment[a]	wt loss (%)	Surface area (m^2g^{-1}) N_2(77K) BET	CO_2(195K) D-P/BET	CO_2(298K) D-P
PSOC 371	1	14.0	1.2	---/ 48	161
	2	11.0	< 1	49/ 36	176
	3	12.4	33	82/ 66	155
PSOC 190	1	13.1	< 1	94/ 66	177
	2	22.0	1.0	213/163	307
	3	24.4	14	303/230	324

[a]1- pyridine extraction at room temperature, 48 hours

2- heating extracted coal in nitrogen atmosphere, 400°C, 4 hours

3- heating extracted coal in oxygen-nitrogen atmosphere, 400°C, 4 hours

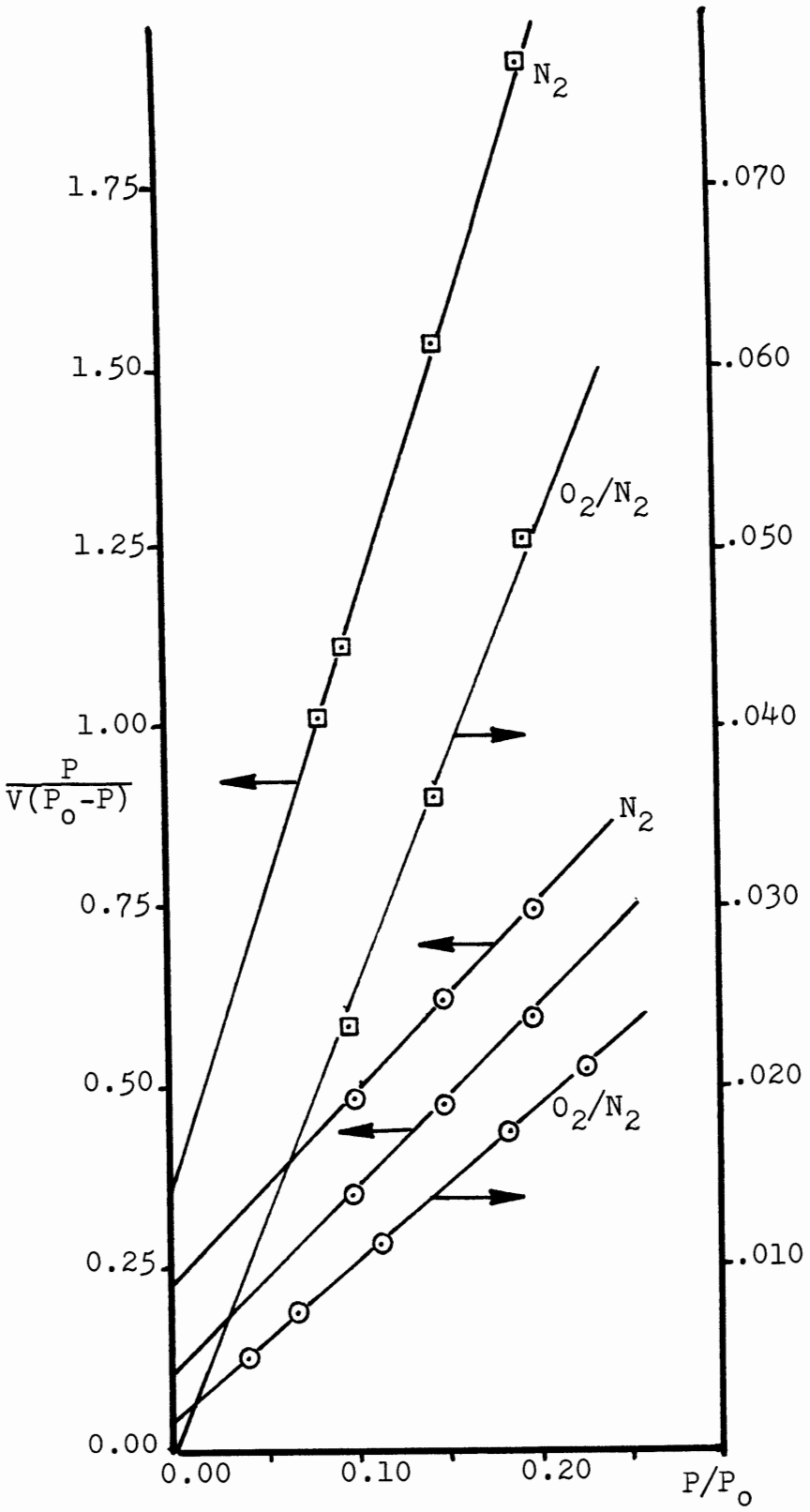

Figure 17. BET nitrogen isotherms at 77 K (⊡) and carbon dioxide at 195 K (⊙). Pyridine extraction and subsequent heating at 400°C, as indicated (PSOC 371).

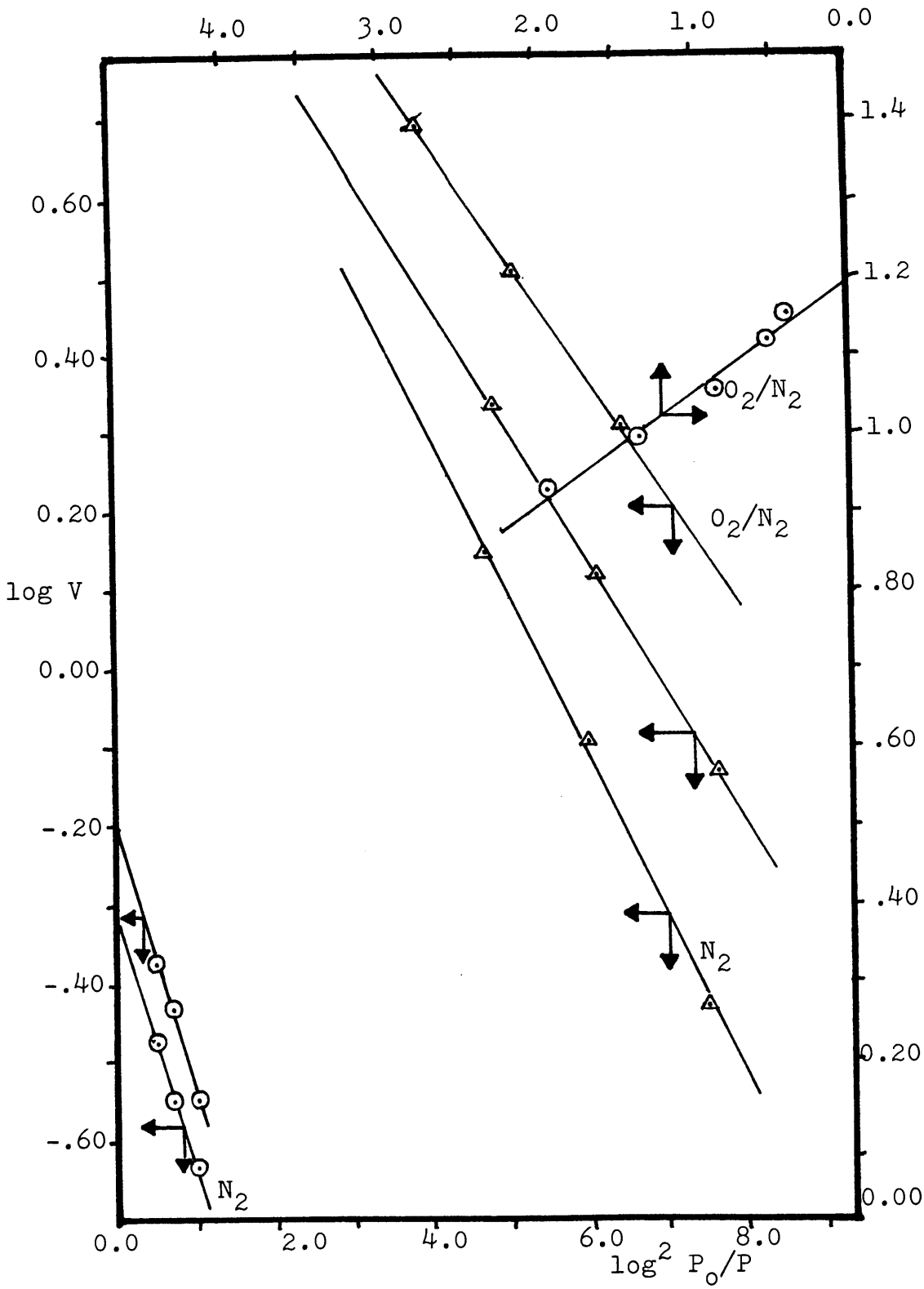

Figure 18. Dubinin-Polanyi carbon dioxide isotherms at 298 K (▲) and 195 K (⊙). Pyridine extraction and subsequent heating at 400°C, as indicated (PSOC 371).

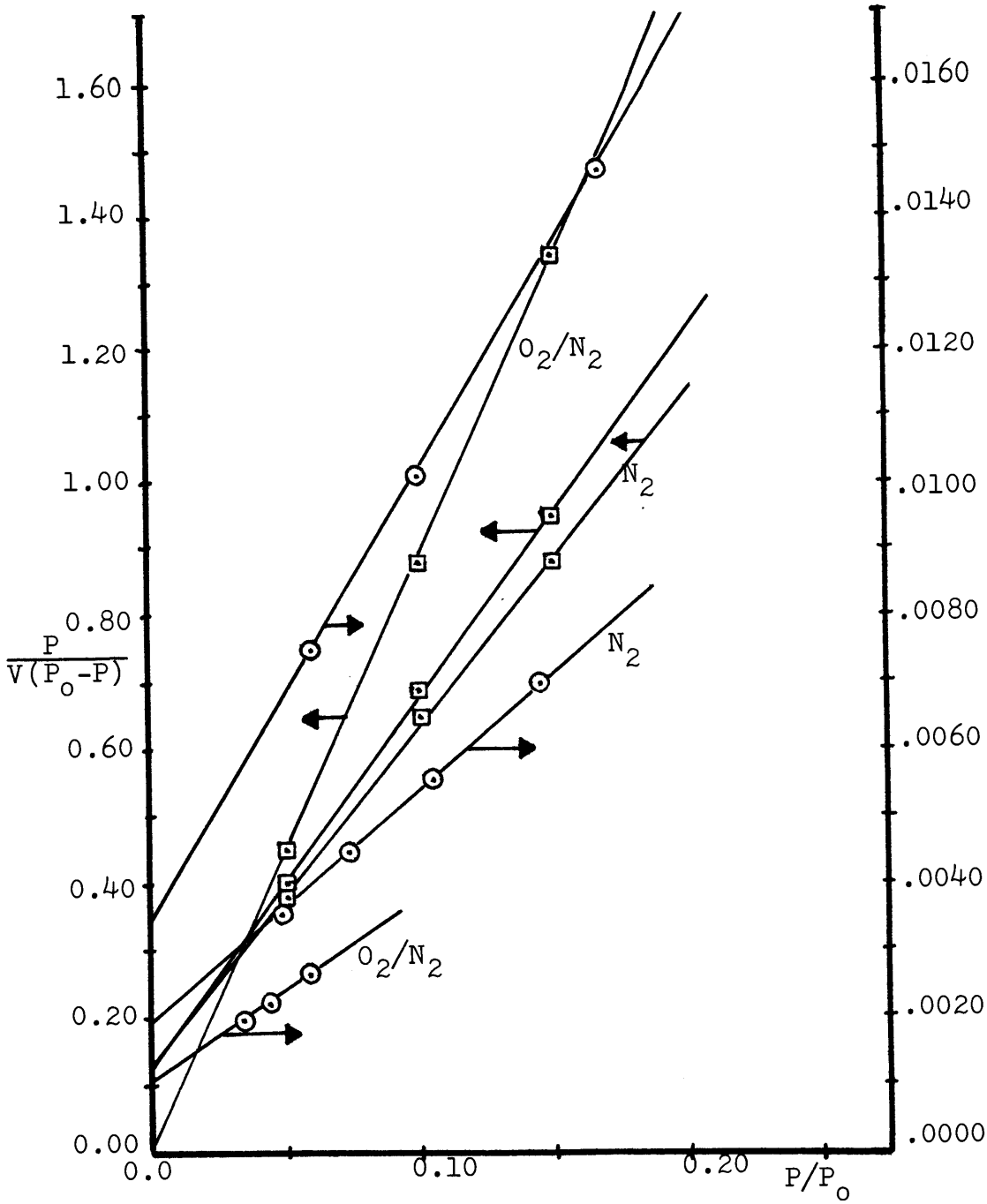

Figure 19. BET nitrogen isotherms at 77 K (⊡) and carbon dioxide at 195 K (⊙). Pyridine extraction and subsequent heating at 400°C, as indicated (PS0C190).

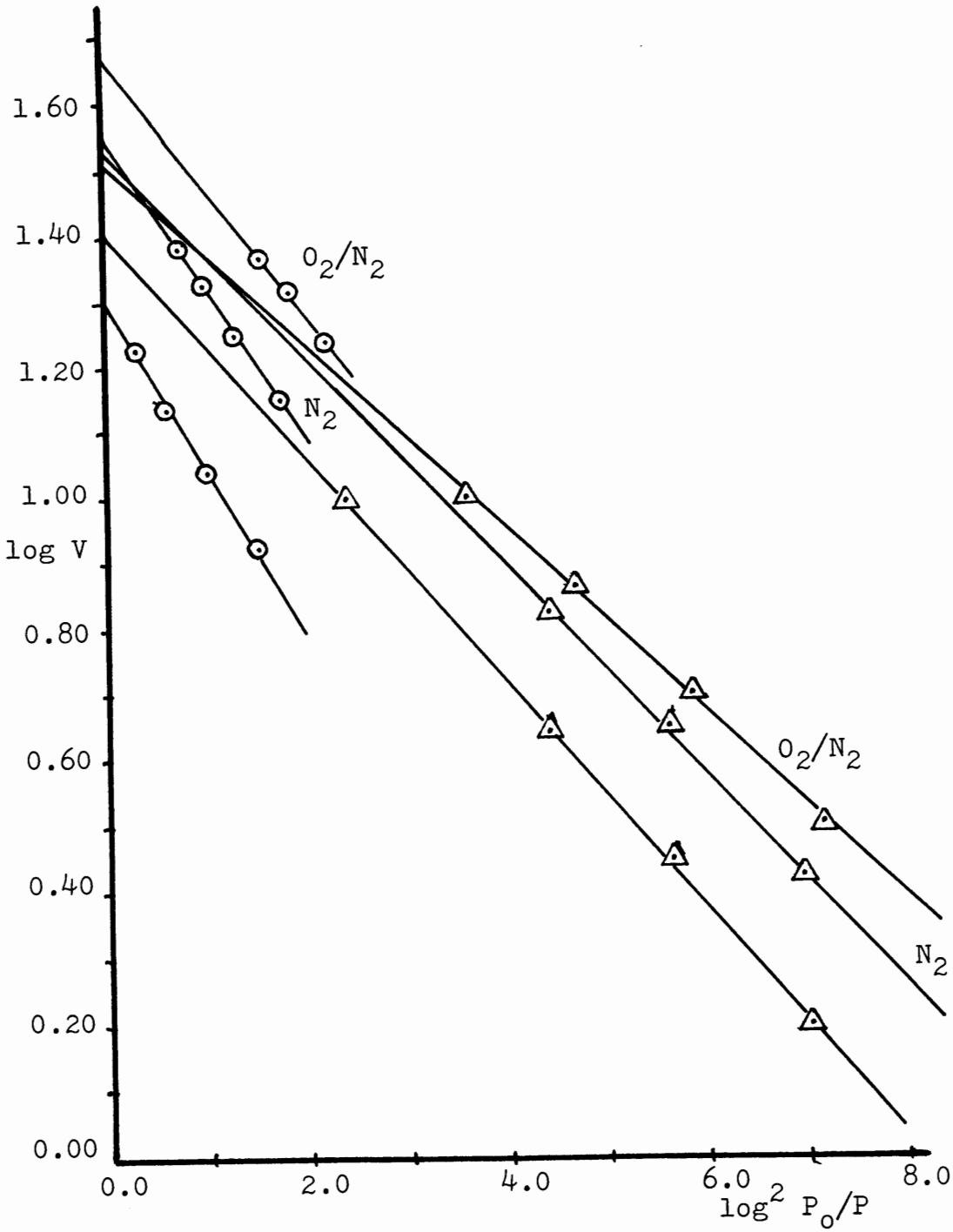

Figure 20. Dubinin-Polanyi carbon dioxide isotherms at 298 K (▲) and 195 K (⊙). Pyridine extraction and subsequent heating at 400°C, as indicated (PSOC 190).

smaller then 0.5 nm in PSOC 371, since the surface area, as measured by CO_2 (298K), increased to 161 m^2g^{-1}, from 90 m^2g^{-1} in the raw coal, but the surface area, as measured by N_2 (77K), decreased slightly. Heating the extracted coal in a nitrogen atmosphere at 400°C has a closing effect on the pores larger then 0.5 nm since the surface area, as measured by N_2 (77K), decreased to less then 1 m^2g^{-1}. The surface area, as measured by CO_2 (298K), increased only slightly, to 176 m^2g^{-1}. Oxidation of the extracted coal in 5%O_2:95%N_2 at 400°C increased the surface area, as measured by N_2 (77K), to 33 m^2g^{-1}, but the surface area, as measured by CO_2 (298K), decreased to 155 m^2g^{-1}. During the oxygen treatment there probably is an increase in the existing pores due to unblocking of blocked pores, however 33 m^2g^{-1} is smaller then the 72 m^2g^{-1} obtained when the raw coal is treated in 5%O_2:95%N_2 at 400°C; hence, pyridine extraction before the oxygen treatment was not beneficial.

The same conclusion is drawn for PSOC 190. Pyridine extraction decreased the surface area, as measured by N_2 (77K), drastically from 29 m^2g^{-1} in the raw coal, to less then 1 m^2g^{-1}. The surface area, as measured by CO_2 (298K), increased only slightly from 169 m^2g^{-1} in the raw coal, to 177 m^2g^{-1}. Therefore, there seems to be a closure of the pores larger then 0.5 nm and not much increase in the smaller pores even though the weight loss is 13.1%. Heat treatment in nitrogen at 400°C significantly increased the sur-

face area, as measured by CO_2 (298K), to 307 m^2g^{-1} but the surface area, as measured by N_2 (77K), is only 1 m^2g^{-1}. Oxidation treatment at 400°C in 5%O_2:95%N_2 increased the surface area, as measured by N_2 (77K), to 14 m^2g^{-1} and to 324 m^2g^{-1} when measured with CO_2 (298K). The N_2 (77K) value is smaller then treating the raw coal in 5%O_2:95%N_2, therefore, the pyridine extraction before the oxygen treatment offers no benefits to increase the surface area, as measured by N_2 (77K). In another project one could try a higher temperature of extraction before the heat and oxidation treatments and try another solvent like tetralin to increase the surface area of coal.

Effect of chromyl chloride on the surface area of PSOC 371 and PSOC 190. The reaction of chromyl chloride with graphite had been reported (29) but not its reaction with coal. In the reaction with graphite, a lamellar compound was formed when graphite was heated with four times its weight of CrO_2Cl_2 at 100°C for 24 hours. The product formed contained 36.3% CrO_2Cl_2 and x-ray studies showed that the carbon planes in the graphite moved apart, from 3.45 to 9 $\mathring{A}^2$. Heating the graphite/CrO_2Cl_2 product between 200° and 300°C caused exfoliation of the graphite, and an increase in the graphite volume. Therefore, it was believed that the same treatment of CrO_2Cl_2 with coal could increase the surface area of the coal.

Table XIII shows the weight change (%) of various heat

treatments along with the surface areas, as measured by N_2 (77K) and CO_2 (298 and 195K), for PSOC 190 and PSOC 371 after CrO_2Cl_2 treatment; included also are the surface area values for the raw coals. The adsorption isotherms are in Figures 21 through 24. It is seen that after the initial treatment with CrO_2Cl_2, both PSOC 371 and PSOC 190 have a weight gain, 2.2% and 16.5%, respectively, and all the surface areas have decreased. For PSOC 371, the surface area, as measured by N_2 (77K), decreased to less then 1 m^2g^{-1} from 1.8 m^2g^{-1} in the raw sample and the surface area, as measured by CO_2 (298K), decreased from 90 m^2g^{-1} to 30 m^2g^{-1}. The surface area, as measured by N_2 (77K), for PSOC 190 decreased from 29 to less then 1 m^2g^{-1} and the surface area, as measured by CO_2 (298K), decreased to 146 m^2g^{-1} from 168 m^2g^{-1}. From the weight gain and the surface area decrease, CrO_2Cl_2 is incorporated into the pore structure of the coal in some manner. The infrared (IR) spectra of the trap contents after heating at 130°C shows CrO_2Cl_2 and some CO_2 for both coals and some HCl for PSOC 371; there could be a little attack of CrO_2Cl_2 with the coal structure.

When the treated PSOC 371 coal is further heated to 337°C, there is a weight loss of 2.2% and the surface area, as measured by N_2 (77K), is still less then 1 m^2g^{-1} but the surface area, as measured by CO_2 (298K), increased to 85 m^2g^{-1}. The IR spectra of the gases in the trap shows HCl and CO_2 were evolved during heating. Heating the treated

TABLE XIII

EFFECTS OF CrO_2Cl_2 TREATMENT FOLLOWED BY HEATING ON THE SURFACE AREAS OF PSOC 371 AND PSOC 190

Coal	Treatment[a]	weight change(%)[b]	Surface area (m^2g^{-1}) N_2(77K) BET	CO_2(195K) BET/D-P	CO_2(298K) D-P
PSOC 371	1	-----	1.8	12.5/16	90
	2	+ 2.2	< 1	3.0/4.7	30
	3	- 2.2	< 1	11/15	85
	4	-15.1	1.0	164/201	244
PSOC 190	1	-----	29	138/193	168
	2	+16.5	< 1	5.7/9.2	146
	3	-11.5	1.5	76/102	247
	5	-13.5	10	253/330	420

[a] 1- raw coal

2- treatment with CrO_2Cl_2, 100°C, 24 hrs., then degassed at 130°C to constant weight.

3- sample from 2 is heated in vacuo at 337°C, 2 hours

4- sample from 3 is heated in vacuo at 450°C, 4 hours

5- sample from 3 is heated in vacuo at 422°C, 4 hours.

[b] + means a weight gain
- means a weight loss
All weight changes are from the previous treatment.

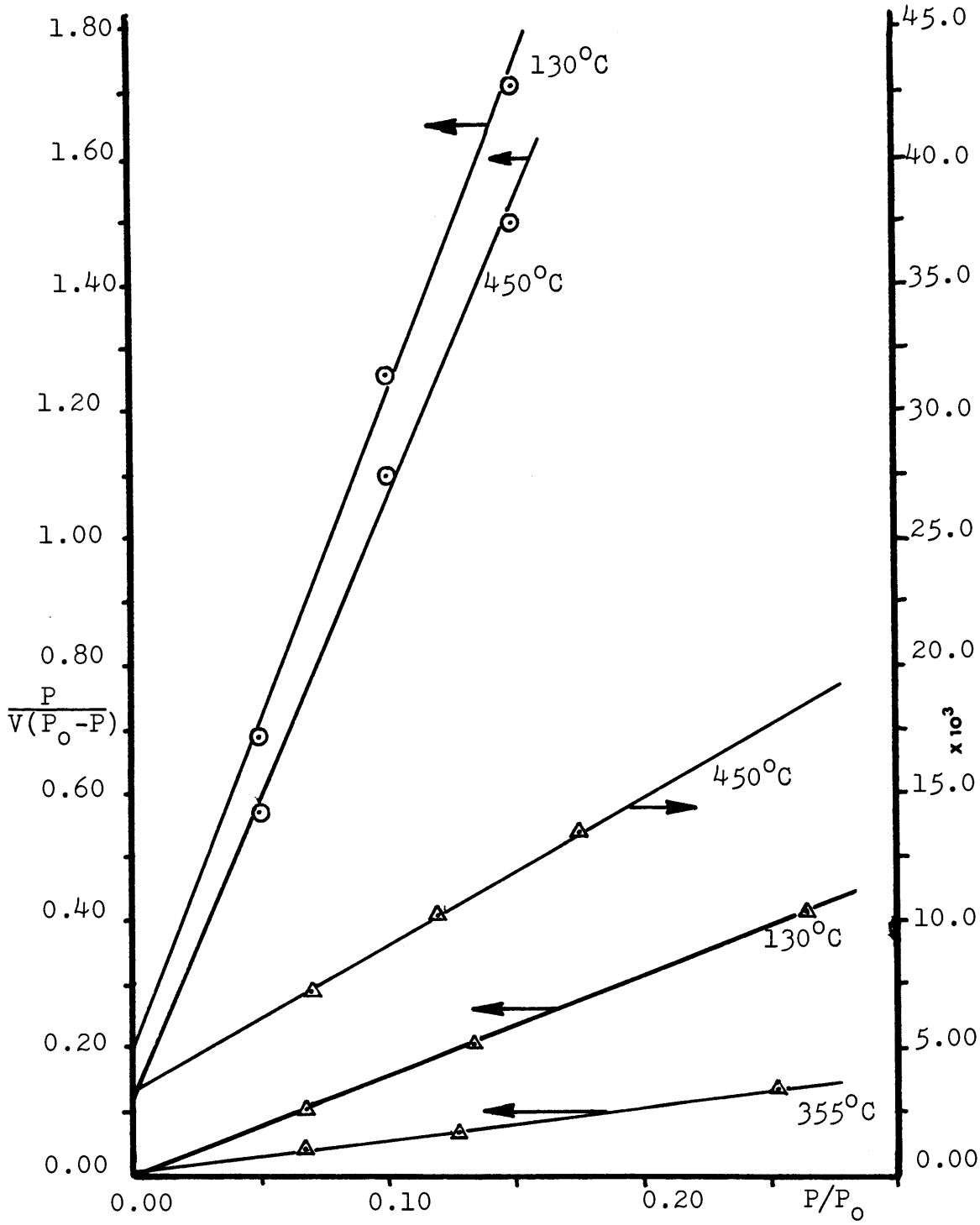

Figure 21. BET nitrogen isotherms at 77 K (⊙) and CO_2 at 195 K (△). Temperature treatment after CrO_2Cl_2 pretreatment (PSOC 371).

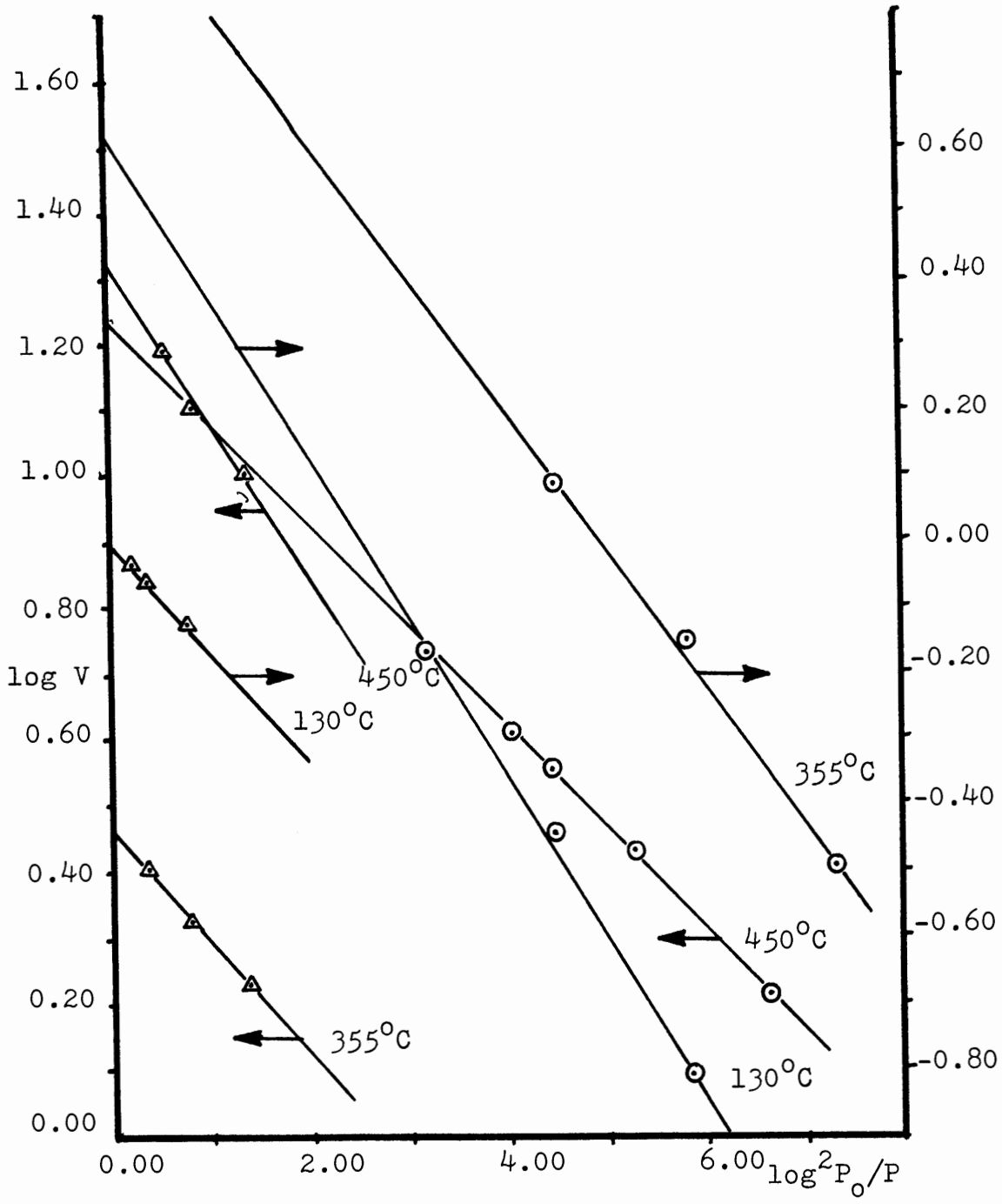

Figure 22. Dubinin-Polanyi CO_2 isotherms at 298 K (⊙) and 195 K (△). Temperature treatment after CrO_2Cl_2 pretreatment (PSOC 371).

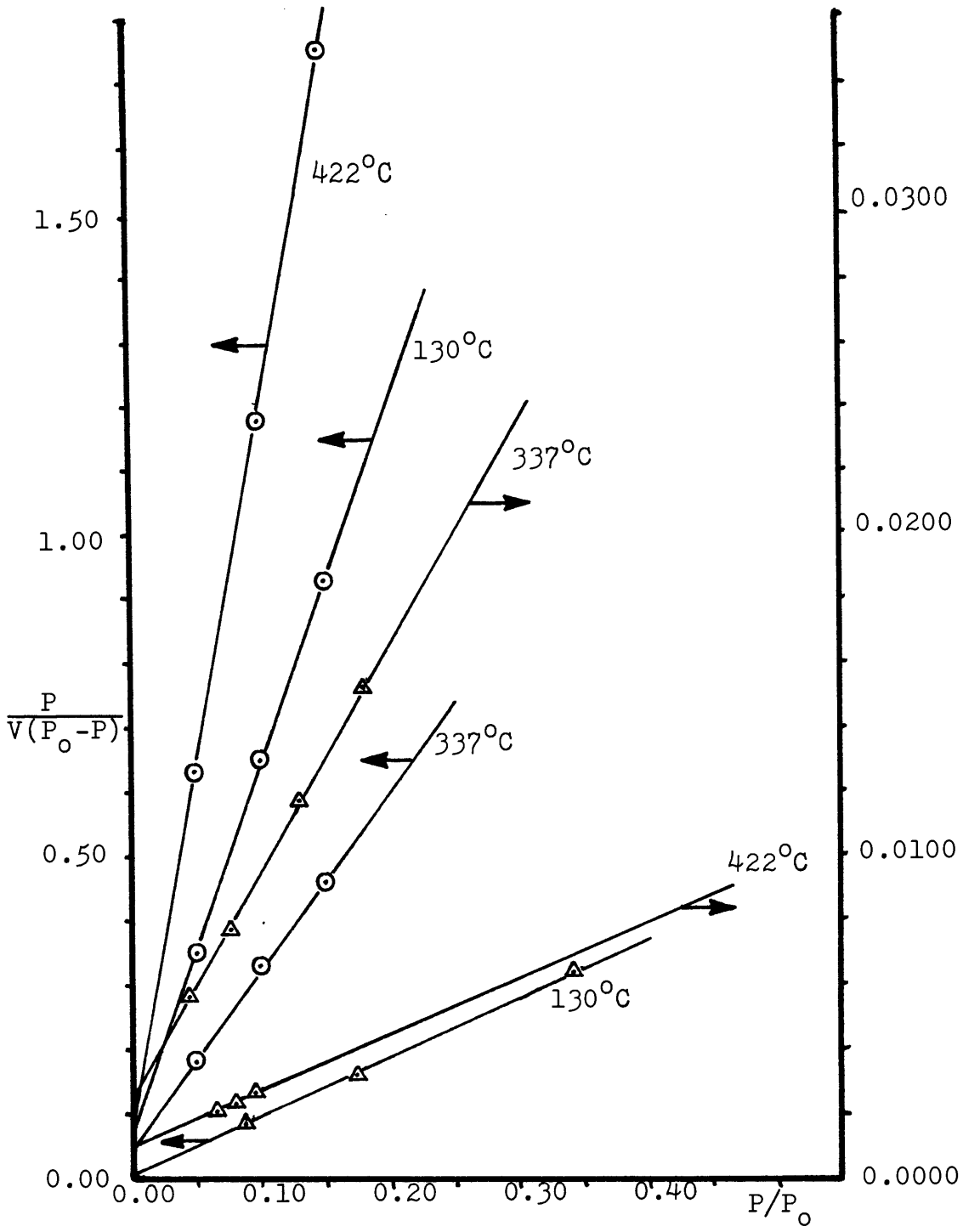

Figure 23. BET nitrogen isotherms at 77 K (⊙) and CO_2 at 195 K (△). Temperature treatment after CrO_2Cl_2 pretreatment (PSOC 190).

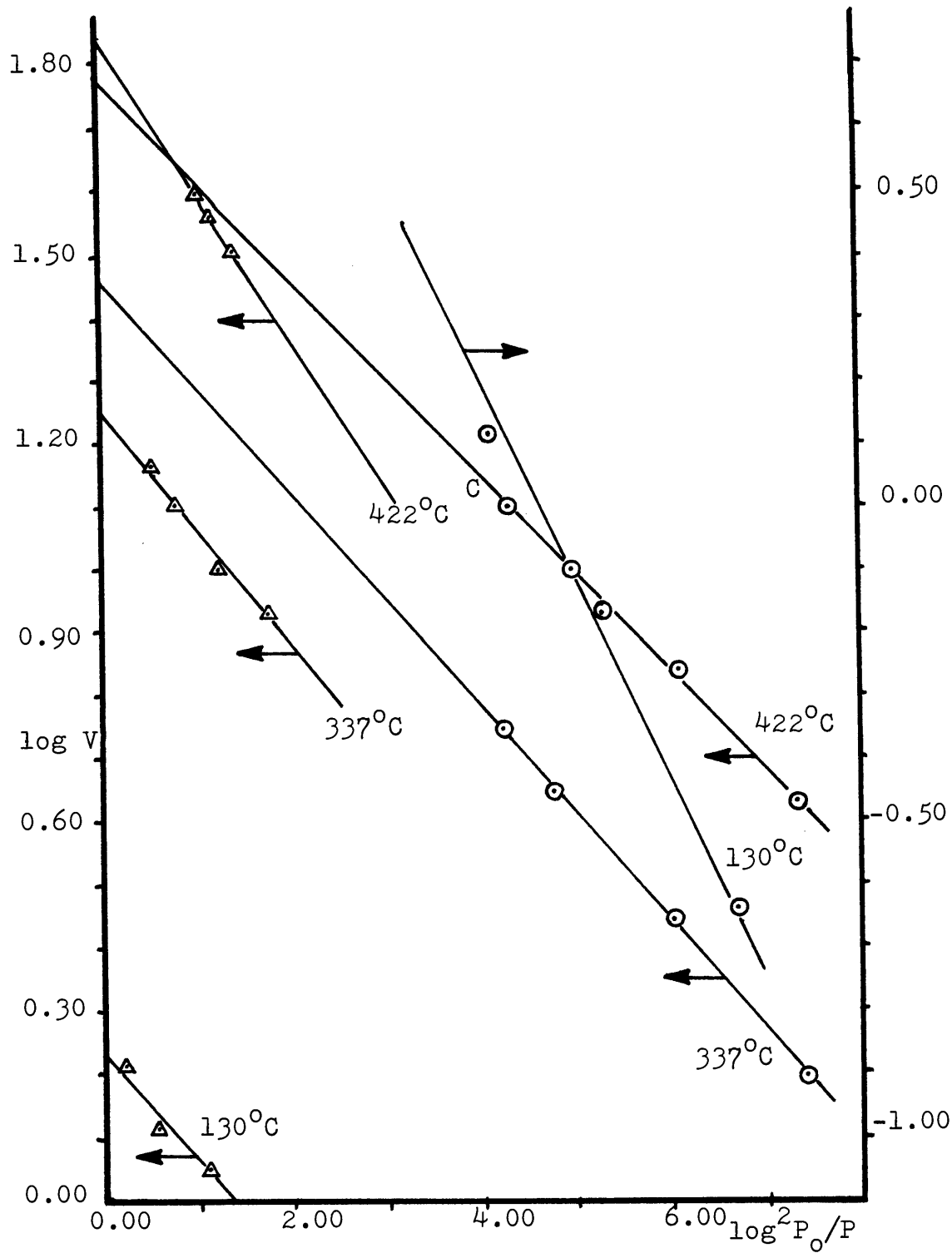

Figure 24. Dubinin-Polanyi isotherms at 298 K (⊙) and 195 K (▲). Temperature treatment after CrO_2Cl_2 pre-treatment (PSOC 190).

PSOC 190 to 337°C gave a weight loss of 11.5% and a slight increase in the surface area, as measured by N_2 (77K), to 1.5 m^2g^{-1}. The surface area, as measured by CO_2 (298K), increased to 247 m^2g^{-1}. The IR spectra of the gases in the trap shows HCl, CO_2 and possibly SO_2 and some low molecular weight hydrocarbons.

Further heating of the treated PSOC 371, at 450°C, produces an additional 15.1% weight loss. The surface area, as measured by N_2 (77K), increased to 1.0 m^2g^{-1} and to 244 m^2g^{-1} when measured by CO_2 adsorption at 298K. The IR spectra of the gaseous contents of the trap, shows CO_2, HCl and some low molecular weight hydrocarbons and possibly some chlorinated hydrocarbons. Heating of the treated PSOC 190 at 422°C, gives an additional weight loss of 13.5% and a surface area, as measured by N_2 (77K), of 10 m^2g^{-1}, which is still less then the raw value of 29 m^2g^{-1}. The surface area, as measured by CO_2 (298K), is increased to 420 m^2g^{-1}. The IR spectra, of the gaseous trap contents, shows CO_2, HCl and again some light hydrocarbons.

From the data above, it is seen that chromyl chloride is incorporated into the coal and that subsequent heating to 422° or 450°C only opens up the pores less then 0.5 nm, since only the surface area, as measured by CO_2 at 298K, increased over the raw value. The CO_2 increase over the heat treatments in nitrogen are only 1.1 and 1.2 times larger for PSOC 371 and PSOC 190, respectively. This method does

not increase the surface area, as measured by N_2 (77K), and therefore is not an advantageous pretreatment process.

Effect of hydrogen and oxygen atoms on the surface area of coals. Previous work using hydrogen atoms reported only the products formed and did not measure any surface area changes (13, 14, 15, 16); therefore, this work was undertaken to see how the surface area was effected by hydrogen and also by oxygen atoms. The experimental method was discussed in the previous section and the results follow.

The results are in Table XIV, for both PSOC 371 and PSOC 190 coals, including the temperature of the sample, time, percent power, weight loss (%) and the surface areas for hydrogen atom treatment. The first location of the microwave cavity was approximately 15 cm above the coal sample but was then relocated to 6 cm above the sample because of poor results, which could be due to a large number of recombination reactions occurring over such a distance. The first three runs for PSOC 371, at room temperature, 90° and 150°C, were exploratory and only the surface area, as measured by N_2 (77K), was measured in order to see if pores larger then 0.5 nm were increased. As can be seen from Table XIV there was no real change in the surface area, as measured by N_2 (77K). The temperature was then increased to 250°C and run for 3 hours. The surface area, as measured by N_2 (77K), still did not increase but now the surface area, as measured by CO_2 (298K), was determined and a value of

TABLE XIV

EFFECT OF HYDROGEN ATOM TREATMENT ON THE SURFACE AREA OF PSOC 371 AND PSOC 190

Coal, location[a], T(°C)	time(hours)	% Power	wt loss(%)	Surface area (m^2g^{-1}) N_2(77K) BET	CO_2(195K) BET/D-P	CO_2(298K) D-P
PSOC 371, 1, room	1	60	0.6	<1	----	---
PSOC 371, 1, 90	1	50	0.6	<1	----	---
PSOC 371, 1, 150	2	50	0.6	1.3	----	---
PSOC 371, 1, 250	3	60	1.9	<1	17/ 23	115
PSOC 190, 1, 400	3	50	9.3	29	158/197	193
PSOC 371, 2, 350	4	50	4.3	<1	16/ 22	155

[a] 1- microwave cavity approximately 15 cm from sample
2- microwave cavity approximately 6 cm from sample

115 m^2g^{-1} was obtained; this is an increase of 25 m^2g^{-1} over the raw coal. The reaction was then tried with PSOC 190 at 400°C for 3 hours and again no change in the surface area, as measured by N_2 (77K), but the surface area, as measured by CO_2 (298K), increased by 25 m^2g^{-1} from the raw coal to 193 m^2g^{-1}. The hydrogen atom treatment was tried once again but at the closer location with PSOC 371 at 350°C; however, the surface area, as measured by N_2 (77K), still did not increase. The surface area, as measured by CO_2 (298K), did increase to 155 m^2g^{-1}, which is 65 m^2g^{-1} over the raw coal.

The evidence from the above data seems to imply that the hydrogen atoms are only affecting the external surface of the coal, where they probably recombine because of some catalytic action, and are not penetrating to the internal pore system. The action on the surface is minimal and creates pores smaller then 0.5 nm and therefore is not a useful pretreatment process.

The results from the oxygen atom treatments are listed in Table XV, all runs are at the 6 cm location, and include the time (hours), % Power, weight loss (%) and the surface areas.

When samples of PSOC 371 and PSOC 379 were left at room temperature, the surface areas changed little from the raw values. The surface area, as measured by N_2 (77K), of PSOC 371 (1 and 4 hour treatments) was less then 1 m^2g^{-1} and the surface area, as measured by CO_2 (298K), changed

TABLE XV

EFFECT OF OXYGEN ATOM TREATMENT ON
THE SURFACE AREA OF COALS

Coal, T(^{o}C)	time (hours)	% Power	wt loss (%)	Surface area (m^2g^{-1}) N_2(77K) BET	CO_2(195K) BET/D-P	CO_2(298K) D-P
PSOC 371, room	1	50	0.81	< 1	12/ 17	105
PSOC 371, room	4	80	1.3	< 1	8.2/ 10	85
PSOC 379, room	4	80	1.2	< 1	40/ 49	250
PSOC 190, 100	2	80	6.1	25	182/200	199
PSOC 190, 100[a]	2	80	7.1	29	159/203	215
PSOC 190, 150[b]	2	80	13.8	29	144/210	184

a- heated in a stream of N_2 at 100^{o}C for 2 hr; wt. loss = 6.5%. Total wt. loss after oxygen treatment = 7.1%

b- heated in a stream of N_2 at 150^{o}C for 2 hr; wt. loss = 7.0%. Total wt. loss after oxygen treatment = 13.8%

from 90 to 85 m^2g^{-1} (PSOC 371, 4 hr) and from 90 to 105 m^2g^{-1} (PSOC 371, 1 hr). For PSOC 379, the surface area, as measured by N_2 (77K), changed from 2.0 to <1 m^2g^{-1} and the surface area, as measured by CO_2 (298K), decreased by only 3 m^2g^{-1} from the raw value to 250 m^2g^{-1}. The weight losses were also small, less then 1.4%. Therefore, the oxygen atoms apparently attack the surface of the coal with little effect in a treatment time up to 4 hours.

PSOC 190 was then treated at 100°C for 2 hours, and a weight loss of 6.1% was observed; however, the surface area, as measured by N_2 (77K), decreased slightly to 25 m^2g^{-1} and the surface area, as measured by CO_2 (298K), increased by 31 m^2g^{-1} to 199 m^2g^{-1}. The question arose as to the significance of the weight loss since there was only a small change in the surface area. PSOC 190 has a high water content, and the weight loss during the treatment could be due to the loss of water and not by the attack of oxygen atoms. To determine this a fresh sample of PSOC 190 was heated for 2 hours in a stream of N_2 and let to cool and weighed. The weight loss after this treatment was 6.5%. Therefore, it was thought that the 6.1% weight loss in the previous run was probably due to loss of water and not caused by oxygen atom attack. The predried sample was then treated with oxygen atoms at 100°C and only produced an additional small weight loss; the total weight loss increased to 7.1%. The surface areas however did not change appreciably.

Another fresh sample of PSOC 190 was taken and degassed at 150°C in a stream of N_2 for 2 hours. The weight loss was 7.0% and with the oxygen atom treatment the total weight loss increased to 13.8%; the surface area, as measured by N_2 (77K), did not change from the raw value and the surface area, as measured by CO_2 (298K), increased by only 16 m^2g^{-1} over the raw coal.

These experiments with oxygen atoms are similar to low-temperature ashing of coals (30, 31). Because of the interest in the mineral matter found in coal, samples were totally ashed (100 hours). Therefore, since there was little surface area change, in a 4 hour treatment, the next thesis project would be to increase the time of treatment and to see if the porosity, and hence the surface area, opens up on prolonged treatment.

Effect of time on the surface areas measured with N_2 (77K). All the treated samples were kept in sample bottles with snap cap or screw lids at ambient temperature. In a carry over from the previous study (17) with PSOC 371, the surface area as measured by N_2 (77K) after 150 days gave a value of 17 m^2g^{-1} and not the 52 m^2g^{-1} reported earlier (17). This led to the question of whether the pore structure changes with time when the samples were left sitting in their containers.

A more in-depth examination of this phenomenon was undertaken with our present PSOC 371 study with oxygen

treatment at 400°C. The results of our study are listed in Table XVI. Initially, the surface area, as measured by N_2 (77K), was 72 m^2g^{-1} and after one month there was virtually no change in that value. However, after 64 days, the surface area, as measured by N_2 (77K), dropped to 42 m^2g^{-1} and after 275 days was down to 25 m^2g^{-1}, where it seemed to level off. The effect could be a result of exposure to oxygen, water vapor or other gases in the atmosphere.

To see whether this was an isolated case, bottles of PSOC 379 run at 400°, 425° and 450°C and PSOC 190 run at 375°, 400° and 425°C in the oxygen-nitrogen treatment were tested after a period of time had elapsed. These results are listed in Table XVI also and their surface area, as measured by N_2 (77K), also decreased. For PSOC 379 run at 400°C, the decrease was from 17 m^2g^{-1} to 9.6 m^2g^{-1} in 134 days; for the 425°C run, the decrease after 126 days was from 49 m^2g^{-1} to 44 m^2g^{-1}; finally for the 450°C run the change was from 120 m^2g^{-1} to 73 m^2g^{-1} in 110 days. For PSOC 190, run at 375°C, the decrease was from the initial 82 m^2g^{-1} to 33 m^2g^{-1} in 130 days; for the 400°C run the decrease was from 87 m^2g^{-1} to 30 m^2g^{-1} in 53 days; finally for the run at 425°C the decrease, in 66 days, was from 37 m^2g^{-1} to 22 m^2g^{-1}. In all seven cases, the surface area, as measured by nitrogen (77K), decreased.

In a separate run, a sample of PSOC 371, 400°C in O_2:N_2 (5%:95%) was sealed in vacuum. The surface area at

TABLE XVI

EFFECT OF TIME ON THE SURFACE AREA AFTER OXYGEN-NITROGEN TREATMENT

Sample	Temperature of treatment (°C)	Surface area* N_2(77K), m^2g^{-1}	Days
PSOC 371	400	72	0
		71	31
		42	64
		25	275
		25	330
PSOC 379	400	17	0
		9.6	134
	425	49	0
		44	126
	450	120	0
		73	110
PSOC 190	375	82	0
		33	130
	400	87	0
		30	53
	425	37	0
		22	66

* Only two measurements were made on the area change with time asmeasured by CO_2 (298K). Coal 371 dropped from 253 to 229 m^2g^{-1} in 456 days; Coal 190 dropped from 321 to 286 m^2g^{-1} in78 days. These are much smaller than the change in area, as measured by N_2 (77K).

this time, as measured by N_2 (77K), was 47 m^2g^{-1}. After 278 days, the cell was opened and the surface area was found to be 42 m^2g^{-1}. A sample of PSOC 371, pretreated at 400°C in O_2:N_2 (5%:95%), when exposed in bottles to ambient pressure and temperature, resulted in the surface area decreasing from 47 to 25 m^2g^{-1}. Apparently, air oxidation with the exposed PSOC 371 results in a lowering of the surface area, as measured by N_2.

Conclusions

1. For all three coals studied, the heat treatments in nitrogen, up to 600°C, significantly increased only the surface area as measured by CO_2 (298 K).
2. Oxygen-nitrogen treatments at 400°C for PSOC 371 and PSOC 190 and at 450°C for 379 significantly increased the surface area, as measured by N_2 (77 K), over the heat treated samples by >80, 19 and 40 times, respectively.
3. Pyridine extraction, at room temperature, before the oxygen-nitrogen treatment did not increase the surface area, as measured by N_2 (77 K), over the oxygen-nitrogen treatment on the raw coals for PSOC 371 and PSOC 190.
4. Chromyl chloride treatment at 100°C with PSOC 371 and PSOC 190 followed by heating, in vacuo, up to 450°C, failed to increase the surface area as measured by N_2 (77 K), over the raw value.

5. Treatment of the coals with hydrogen and oxygen atoms failed to produce any significant change in the surface area.
6. Samples left at ambient conditions, after the oxygen-nitrogen treatment, had the surface area, as measured by N_2 (77 K), decrease as the time increased; this was probably due to air-oxidation and closure of the larger pores.

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